PROCESS SYNTHESIS AND EXPERIMENTAL ANALYSIS OF WASTE TIRE THERMOCHEMICAL CONVERSION PROCESSES

by

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Process synthesis and experimental analysis of waste tire thermochemical conversion processes.

I declare that the above thesis is my own work and that all the sources that I have used or quoted have been indicated and acknowledged by means of complete references.

I further declare that I submitted the thesis to originality-checking software and that it falls within the accepted requirements for originality.

I further declare that I have not previously submitted this work, or part of it, for examination at Unisa for another qualification or at any other higher education institution.

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ABSTRACT

Title of Document: **Process synthesis and experimental analysis of waste tire thermochemical conversion processes**.

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The thermochemical conversion of waste tires for chemicals and power production is investigated using process synthesis techniques and experimental analysis. Pyrolysis and gasification technologies were evaluated in terms of the fundamental thermodynamic metrics of carbon efficiency, atom economy, e-factor and chemical potential efficiency, thermal efficiency and their market-related revenue potential. The synergetic effect of co-gasification and co-pyrolysis of waste tires with alternative waste materials is also evaluated experimentally. The thermodynamic analysis found that pyrolysis pathways perform better in terms of thermodynamic efficiency and carbon footprint than gasification processes, which lose about 45% of the carbon feed to carbon dioxide. However, the gasification routes offer higher potential revenue, yielding as much as \$625 per ton of waste tire as compared to \$205 from the pyrolysis route. It was also found that waste tire integrated gasification combined cycle (IGCC) net-work output is 10.5 GJ/ton of tire much higher than that of conventional coal IGCC at 9.6 GJ/ton of coal. The results of the techno-economic analysis showed the feasibility and sustainability of operating a 550-tonne-per-day plant producing methanol or electricity requires a minimum government subsidy of 0.115 \$/kg to make the process economical and cost competitive to fossil-fuelled plants. With the levy, the minimum selling price for electricity would be \$ 0.098/kWh and that of methanol at \$420/ton. The results reported here clearly demonstrate the synergistic capabilities for integrating waste materials such as gypsum and spent fluid catalytic cracking (FCC) catalyst in tire recovery facilities to recover valuable products and reduce the carbon footprint via catalytic CO_2-assisted gasification. The findings of this dissertation indicate that, from an environmental aspect, converting waste tires to transportation fuels is more desirable than landfilling them, and that gasification technologies may offer better long-term prospects than pyrolysis, despite their higher emissions. Globally, fossil fuels are currently being burned, and it has been demonstrated that waste tires potentially perform as well as or better than existing fossil fuel processes; therefore, there is still a strong environmental justification for the usage of waste tires.

Keywords: Waste tires, pyrolysis, gasification, thermodynamic analysis, spent Fluid Cracking Catalyst (FCC), Catalytic CO_2-gasification, in-situ and quasi-in-situ catalytic pyrolysis, Techno-economic analysis.

LIST OF PUBLICATIONS AND CONFERENCE PROCEEDINGS

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1 Introduction

1.1 Contextual background

In 2022, the United Nations announce that the world population has reached eight billion [1]. With this increase in the global population, as well as the required industrialization to sustain the population, the requirements for energy has accelerated. This increase in energy demand has led to a rapid decline in the fossil fuels level, while contributing to increase global emission and waste generation. This has amplified the interest in energy diversity and renewable sources of energy that can displace the traditional fossil fuels to decrease the elevated accumulation of greenhouse gases in the environment [2]. Given the rapidly increasing demand for fossil fuels in many emerging economies, sustainable sources of new and advanced bio-based products may be the only viable way to meet the needs of populations in such markets [3]. Furthermore, by using waste as feedstock in the production of energy and other chemicals can achieve significant saving in greenhouse gas emissions compared to single production from fossil fuels.

South Africa generates over 55 million tonnes of general waste per annum of which 65% is landfilled, 34% is recycled and 0.2% fraction is stockpiled [4]. Further analysis shows that 50% of the general waste is organic waste. The organic waste has potential in the production of energy and other chemicals. One such organic waste with an energy content comparable to coal is waste tires. Waste tires generation in South Africa is one of the issues that have not found a sustainable solution yet. The estimated annual flow of waste tires is set to be between 250 000 and 300 000 tonnes [5]. This adds to an already existing stockpile of 900 000 tonnes spread across 26 national storage depots without a solid plan for reprocessing or recycling. The recycling rate for waste tires in South Africa is approximately 20% as compared to close to 100% in Europe and 91% in the United States. South Africa thus urgently needs to create an enabling environment for increased reuse, re-treading, energy and material recovery from waste tires. In South Africa 32% of the 54000 treated waste tires were utilised for energy recovery and 58% for material recovery. Figure 1.1 shows the most dominant methods used for waste tyre management in South Africa.

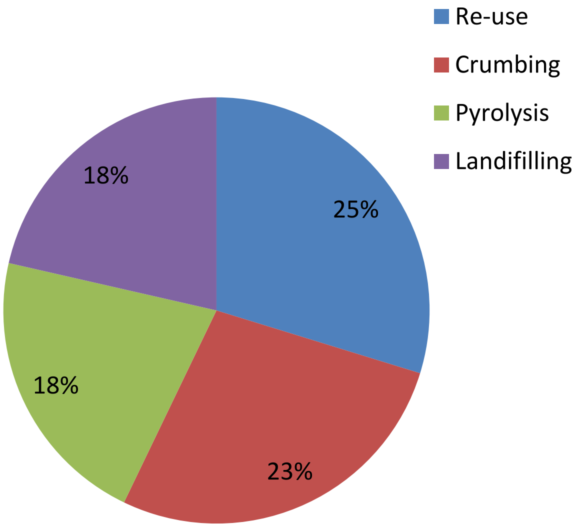

Figure 1.1: Waste tyre recycling methods [6]

To reduce the annual generated waste and stockpile, the waste tire processing capacity of South Africa must be expanded. In 2022 a new waste tire management plan (IndWTMP) was released [5]. The vision and mission of the (IndWTMP) is to achieve 80% processing/recycling capacity of the annual generated waste by 2035 and 90% reduction of the current stockpile by 2038. The achieve this, the IndWTMP advises to use the incentives developed by the government to create additional processing capacity by upscaling or increasing capacity of existing processing facilities where feasible; and establishing new processing capacity. In other words, the government must subsidies new plant establishment, equipment upgrades, grants on a cost-sharing basis.

Due to the high demand for energy and poor uptake of other recycling alternatives for tires, energy recovery is still a better option to handle the rising stockpile of waste tires [7]. For example, in an incineration process, waste tires can be combusted and reduced in volume by up to 90% and in weight by up to 70% [8]. In these facilities waste tires are converted to heat, ash, CO_2, and various air toxins. However, due to stringent emissions regulations, lack-of community acceptance of incinerators, high capital costs, there is little interest in building more facilities. Currently waste tires are used in cement kilns and paper mills to replace about 25% of the coal. Other methods of energy recovery are available that unlike combustion can convert waste tires to valuable chemicals, these technologies include gasification, pyrolysis, flash pyrolysis, and liquefaction. These technologies have an advantage in that they are net energy producers with possible valuable chemicals recovery; they non-polluting and capable of destroying most of the organic substances, which are harmful to human health [8]. In this study focus is given to pyrolysis and gasification technologies for sustainable utilization of waste tires. Exhaustive literature exists on the utilization of pyrolysis and gasification of wase tires for material and energy recovery [9–11]. A published literature study conducted by the author [12], discussed later in chapter 2 came to flowing conclusion: Waste tires fall in the category of waste that is exceedingly difficult to recycle. Under thermal treatment waste tires produce a huge product spectrum that require extensive downstream processing. Four categories of products are produced mainly gas, liquid oil and char and ash. The liquid phase mainly called the tire-derived-oil (TDO)/tire pyrolytic oil (TPO) is a complex mixture of aromatic hydrocarbons, n-paraffins and olefins terpenes, mono and poly aromatics, nitrogen and sulfur containing heterocycles and oxygenates [13,14]. The solid fraction called char is a mixture of carbon black and other inorganic substances such as zinc, sulfur, silica, and clay and has very poor surface area and pore sized to be considered activate carbon. The gas phase is mostly a mixture of over 25 non-condensable light hydrocarbons (C1-C5), hydrogen, CO_x, and sulfur compounds (SO_x and H_2S) [15].

Efficient conversion of waste tires to produce energy or chemicals requires understanding the limits of performance in terms of what is achievable at what energy or emissions cost. Tires are made up of mostly carbon and hydrogen at a molar ratio of roughly 1:1. This ratio sets certain limits to the type and amounts of products to which tires can be chemically converted. So far, there is no systematic method for determining these limits. The current research focuses on pyrolysis and gasification and can be divided into two. The first is experiments studies that investigate the optimum operating conditions to target specific products, during thermal treatment. This often this involves investigating the key parameters such as temperature, catalysts, residence time, oxidizing agent, reactor configurations feeding ratio and co-feeding with another feedstock to maximize a specific product. The second is the use of theoretical analysis to investigate the decomposition behavior and kinetics of waste tire decomposition, as well thermal and exergy efficiency of a tire thermochemical conversion process. The approach often involves selecting the product, the reactions that can yield this product from tires and finally selecting the unit operations. Following the completion of these procedures, mass and energy balances are performed on the process. The cold gas efficiency is then used as the measure of performance. In both cases the current research focus on optimizing the reactor. Then other downstream or connecting units are integrated later. The problem with this approach is that the performance of the process is already pre-determined by the choice of the product and the type of process (Pyrolysis or gasification) and the operating conditions, which also place the optimization in a narrow range. Furthermore, optimizing one part might place excessive strain on subsequent parts, which can subsequently affect the whole optimization process [16]. For instance, in the current literature we have identified that the generation of CO_2, soot and tars are still a major barrier to the commercialization of waste tire thermal processes and little improvement have been achieved through catalysis and optimization of the reactors. One may ask whether these unwanted products are inevitable during the thermal processing of tires. This work presents a method that can answer such a question by determining the limits of performance of the process and can graphically reveal opportunities to improve the process from a material and energy perspective. Furthermore, the one aspect identified is that current research only focuses on investigating key operating parameters such as temperature, pressure, feed ratios, etc. on the desired product selectivity. The penalty or negative effects on the overall system performance to meet such operating conditions are not investigated. For example, it is recommended that the operating temperature for the gasification of tires to syngas should be 750-950ºC. However, one needs to ask how these temperatures (heat) will be met. And once the heat is integrated into the process how does this affect the overall efficiency of the process. Fox [16], showed that carbon dioxide production is linked to the flows of heat and work in a process. Minimizing the loss of heat and work during its operation the negative environmental impact on the surroundings will be reduced. One must always consider the connection and interactions between unit operations of the system to achieve the global optimum. Therefore, the analysis of waste tire conversion processes must be looked at from a system point of view to determine the limits of performance and reveal opportunities for optimized processes. Such work would be innovative in that it will contribute to the development of a systematic design methodology for waste tire recycling and evaluate existing processes from a fundamental mass balance and thermodynamic point of view.

The approach adopted in this work can address some of the topics that has not been covered yet in waste tire conversion research. These include:

1. Co-gasification of tires with other feedstock can unlock the reactivity of tire char and consume tar.
2. Unveiling opportunities for process routes to convert tires to value-added products. Much of the research focuses merely on syngas as intermediate raw material, however by evaluating the overall process, one may reveal opportunities for co-generation, material and energy integration, and cost savings.

3. A system view of waste tire processing that can systematically target optimized processes. Overall system analysis uses thermodynamics to determine the limits of performance in terms of the material going in and out of the process as well as the energy, both in quantity and quality, involved in the transformation. The goal is to optimize the system rather than focusing on the small details of individual units.

Key questions to be addressed when evaluating waste tires as raw material for energy and material recovery are:

1. What are the performance limits in waste tire conversion to chemicals and energy from the material and energy point of view? For example, many investigations on syngas production from tires have been conducted. However, many of these works have overlooked the unavoidable CO_2 emission which in some cases can be comparable to that of coal. One may ask whether there are better options than syngas or whether co-production or polygeneration of other products may prevent CO_2 emissions.

2. What are the highest-value process pathways for the chemical conversion of tires?

3. What is the commodity value of waste tires as an energy material?

This work is an attempt to process intensification of and improvements of mass and energy efficiency for waste tire conversion. The system's approach adopted in this study is similar to the work published by Bilal [17], Sempunga [18] and Fox [16]. This project's primary objective is to systematically build carbon-efficient and energy-efficient waste tire conversion processes. The work will investigate thermochemical conversion processes viz. gasification, pyrolysis, integrated gasification combined cycle (IGCC), as well as synergy of polygeneration of products from a combination of multi-processes. The goal is to find the most desirable means of recovering energy and products from waste tires. The approach used in this work to develop the systematic design methodology for waste tire conversion is different from the methods described in the literature, i.e., single unit operation optimisation where the feed and products have already been decided upon which leaves little room for optimization. The present work proposes a holistic method for waste tire conversion which enables visualizing all possible outcome from a given feed, constituting a region, which we call the attainable region, within which the most efficient processes can be explored, and targets can be set before the process is designed. Numerous alternatives can be simultaneously scanned and evaluated according to some performance criteria which could include carbon efficiency and energy efficient including thermal and second law efficiency. This contribution has the potential to improve the environmental as well the economic aspect of waste tire conversion due its potential to improve the product quality, the energy efficiency and minimizing waste products. This is demonstrated by looking at selected process targets for which flowsheets are developed and then evaluated from the material, thermodynamic and economic perspective.

1.2 Aims and Objectives

The aim of the research:

1. Use the fundamental concepts of thermodynamics to synthesize processes that can unlock the potential of waste tyres for the efficient production of energy and chemicals.
2. Apply the Integrated Process Synthesis tool to provide insights and set targets for the overall processes based on fundamental concepts. The focus will be on the process that requires carbon as feed.

The main objectives of this research are to:

1. A detailed literature review of waste tyre thermochemical conversion processes.
2. Apply the GH-space graphical technique that uses fundamental properties of enthalpy and Gibbs free energy to develop the thermodynamic attainable region of waste tyre valorization processes.
3. Identify performance targets and develop various process flowsheets to meet the targets identified from the region.
4. Use Aspen plus to simulate the optimal tyre conversion process targets.
5. Conduct a techno-economic analysis of the processes developed to assess their profitability.
6. Design experiments to validate simulated results from objective 1 to 4.

1.3 The Approach

Due to the stringent environmental regulations, chemical engineers are faced with the challenge of developing new alternative technologies and methods that make the best use of raw materials and energy as they possibly can. Such new technologies must minimize the environmental impact but must remain profitable. It has been shown that the greatest opportunities to innovate and improve are also most prevalent at the earliest stages of design, during research/development, or the conceptual design stage before the flowsheet exists [19]. Opportunities for innovation decrease as the design proceeds, and once a plant has been put into operation, it is very costly to attempt a retrofit [16]. Synthesis and analysis are the two key steps chemical engineers use to create structures for systems to convert raw materials into useful products. In the analysis approach, an existing or predetermined process structure is used together with given inputs for determining the outputs. This approach is often used for modelling and conducting a sensitivity analysis of impact variables to a given process through simulations [19]. However, this approach relies on human experience and adaptations of previous designs and flowsheets which may have been flawed and this limits the ability to innovate. This approach tends to inherit the strengths and weaknesses of what came before and accomplish nothing new [16]. A high-level process synthesis tool has been developed [19] which can determine the structure of the process by only knowing the inputs and what the desired outputs should be from the process.

In this section, we would like to determine the attainable region for waste tire chemical conversion into various products. The attainable region will provide information on the performance limits of the process from the material and energy perspectives. The limits of performance can be understood as the extreme points that any tire chemical conversion process can achieve. Although these points are theoretical limits, real processes will always perform below these limits. Given a feed composition of a waste tire, a conversion process, and a set of species that are involved in the process, we can determine all possible composition states that can result from the chemical conversion of the tires into the specified species. This involves finding a solution for the number of moles of each species subject to a defined set of constraints depending on the number of degrees of freedom for the system.

For a *chemical system* containing N species and M elements, denoted as $\{(A_1, A_2, \ldots, A_i, \ldots, A_N), (E_1, E_2, \ldots, E_k, \ldots, E_M)\}$ where A_i is the elemental formula of species i and E_k is the kth element in the system. The order in which the species and elements are presented in the system is not important for the attainable region, however, once decided upon, it must be kept consistent during the derivation as most the equations are written in matrix form.

The *element-abundance* constraint is one of the constraints that must always be satisfied as it constitutes the basis for the material conservation within the system. The element abundance equation can be written in vector-matrix form as follows:

$$\mathbf{An} = \mathbf{b} \tag{1}$$

Where:

- $\mathbf{A}$ is the *formula matrix* an $M \times N$ matrix containing the amount of each element in each species where M is the number of elements and N is the number of species in the system.

- $\mathbf{n}$ is the *species-abundance* vector $(N \times 1)$containing the number of moles of each species in the system.

- $\mathbf{b}$ is the *element-abundance* vector containing the total amount of each element available in the system.

When we consider the change in moles or the net number of moles for each species from one composition state to another, eq.1 becomes:

$$\mathbf{A}\,\boldsymbol{\delta}\mathbf{n} = \mathbf{0} \tag{2}$$

Where $\boldsymbol{\delta}\mathbf{n}$ is the net species-abundance vector and is given by:

$$\boldsymbol{\delta}\mathbf{n} = \mathbf{n}^{(2)} - \mathbf{n}^{(1)} \tag{3}$$

The superscripts (1) and (2) in eq.3 denote state 1 and state 2 respectively.

Given the initial number of moles of all the species (or the initial species-abundance vector) $\mathbf{n}^{\boldsymbol{o}}$, the element-abundance vector $\mathbf{b}$ is fixed and is given by $\mathbf{b} = \mathbf{A}\mathbf{n}^{\boldsymbol{o}}$. Therefore, the element-abundance constraint can also be written as follows:

$$\mathbf{An} = \mathbf{A}\mathbf{n}^{\boldsymbol{o}} \tag{4}$$

The compositional state $\mathbf{n}$ of a system can be expressed in terms of an initial compositional state $\mathbf{n}^{\boldsymbol{o}}$ as follows:

$$\mathbf{n} = \mathbf{n^o} + \sum_{j=1}^{R} \boldsymbol{\nu_j}\xi_j \qquad (5)$$

where $\boldsymbol{\nu_j}$ is the stochiometric vector such that:

$$\mathbf{A}\boldsymbol{\nu_j} = \mathbf{0};\ (\boldsymbol{\nu_j} \neq 0)\ ;\quad j = 1, 2, \ldots, R \qquad (6)$$

Thus $\boldsymbol{\nu_j}$ is any set of R independent solutions that satisfies eq.6. Therefore, R is the maximum number of linearly independent solutions for eq.6. It is given by:

$$R = N - C \qquad (7)$$

Where;

$$C = \text{rank}\,(\mathbf{A}) \qquad (8)$$

and N is the number of columns of the formula matrix $\mathbf{A}$, it is also the number of species in the chemical system.

We therefore define the matrix **N**, an $N \times R$ matrix, as the *complete stoichiometric matrix* whose R columns are linearly independent vectors $\boldsymbol{\nu_j}$. And therefore eq. 6 can be written as single matrix as follows:

$$\mathbf{AN} = \mathbf{0} \qquad (9)$$

where $\mathbf{N} = (\boldsymbol{\nu_1}, \boldsymbol{\nu_2}, \ldots, \boldsymbol{\nu_R})$.

The vector $\boldsymbol{\nu_j}$ contains the stoichiometric coefficients of the $\boldsymbol{j}$th chemical equation. Therefore, for any chemical system there are only R independent chemical equations that represents all possible compositional states of the system.

From eq.6, a complete set of $\boldsymbol{\nu_j}$ (also written as **N**) is not unique but can be any set that satisfies eq.6 (or eq.9). Therefore, the set of independent chemical equations derived from the stochiometric vectors do not represent any *chemical reactions* occurring in the system but are simply algebraic solutions of all possible composition states that any chemical reactions path can achieve. Thus, to distinguish *a chemical equation* from a *chemical reaction*, we use the equal sign (=) instead of an arrow (→).

The quantities ξ_j in eq.5 are a set of parameters, which determine the linear combination of the coefficient vectors $\boldsymbol{v_j}$ required to achieve a particular compositional state $\mathbf{n}$. Thus, the number of moles of each species at a compositional state is given by:

$$n_i = n_i^o + \sum_j^R v_{ij}\, \xi_j \tag{10}$$

where v_{ij} is *the stoichiometric coefficient* of ith species in the jth stoichiometric vector, and ξ_j is the parameter for the jth stoichiometric vector.

The *Attainable Region* (AR) for the chemical system is defined by the sets of ξ_j's for which the number of mole of each species is positive. Thus, the AR is obtained by using eq 10 as an additional constraint when written as an equality as follows:

$$n_i = n_i^o + \sum_j^R v_{ij}\, \xi_j \geq 0 \tag{11}$$

One can also formulate a linear programming problem to determine the attainable region as follows:

$$\text{find all } \xi_j \quad , \qquad \text{subject to} \begin{cases} \mathbf{n} = \mathbf{n}^{\boldsymbol{o}} + \sum_{j=1}^{R} \boldsymbol{v_j}\xi_j \geq 0 \\ \mathbf{An} = \mathbf{An}^{\boldsymbol{o}} \end{cases} \tag{12}$$

Eq.12 is a linear programming problem whose vertices constitute a convex connected region in the ξ space of dimension R. It can also be transformed into the n_i space of dimension N.

If there are K extreme points in the attainable region, we can denote the set of these vertices in the ξ space as $\boldsymbol{\xi_V}$ $(\boldsymbol{\xi}_{V_1}, \boldsymbol{\xi}_{V_2}, \dots, \boldsymbol{\xi}_{V_k})$, where $\boldsymbol{\xi}_{V_k}$ is the parameter vector at the **k**th vertex. Similarly, in the n_i space as we denote $\mathbf{n}_V$ $(\mathbf{n}_{V_1}, \mathbf{n}_{V_2}, \dots, \mathbf{n}_{V_k})$, where $\mathbf{n}_{V_k}$is the composition vector at the **k**th vertex of the AR.

Another way of visualizing the AR is to transform its vertices into a two-dimensional space of Gibbs Free Energy and enthalpy as follows:

$$\left.\begin{aligned}\Delta G_{V_k} &= \sum_{j=1}^{R} \xi_{jV_k} \boldsymbol{\nu_j} \widehat{\boldsymbol{G}}^{\boldsymbol{T}} \\ \Delta \mathrm{H}_{V_k} &= \sum_{\boldsymbol{j=1}}^{\boldsymbol{R}} \xi_{jV_k} \boldsymbol{\nu_j} \widehat{\boldsymbol{H}}^{\boldsymbol{T}}\end{aligned}\right\} \quad (13)$$

Where $\widehat{\boldsymbol{G}}$ and $\widehat{\boldsymbol{H}}$ are the molar Gibbs free energy and molar enthalpy vector for the species.

1.4 Structure of the dissertation

The current dissertation consists of 10 chapters. It is important to highlight that this work is provided as a series of articles. As a result, there will be some duplication, particularly in regard to statistical information on discarded tires as well as the theoretical formulation of the used thermodynamics and experimental design. Each article may, if wanted, be read separately of the others.

In **CHAPTER 2** (Literature review), details the current studies associated with thermochemical conversion of waste tires. Progress in conventional waste tire pyrolysis reactors, reaction conditions, catalyst, product fractions and efficiencies are reviewed. Trends in conventional gasification routes such as Integrated Gasification Combined Cycle (IGCC), co-gasification and catalytic gasification are also presented. The chapter concludes by presenting evidence showing that there is insufficient literature data on techno-economic analysis on gasification/co-gasification of waste tires and sola assisted processes to determine the highest value process pathways for chemical conversion of tires. Also, a system analysis approach is required to determine the limits of performance of these processes in terms of the material going in and out of the process.

CHAPTER 3 compares the pyrolysis and gasification pathways in terms of the fundamental thermodynamic metrics of carbon efficiency, atom economy, e-factor and chemical potential efficiency, and also their market-related revenue potential to determine their economic favourability and environmental impact.

In **CHAPTER 4** and **CHAPTER 5** we use experiments to evaluate the synergy of co-gasification of waste tires with other waste materials and catalysts. Waste gypsum from the construction and development sector as well as the fluid catalytic cracking FCC catalyst are used to improve the yield of syngas during gasification and pyrolysis of tires. In **CHAPTER**

6 mass, energy and work balances as well as Aspen Plus are used to analyse the performance of a waste tire IGCC plant. The effect of operating parameters such turbine compression ratio, combustion temperature, and gasification temperature are evaluated with respect to thermal and work efficiency. **CHAPTER 7, CHAPTER 8** evaluates the production of methanol and power from waste tires. The results show from an environmental standpoint, converting waste tires to methanol is preferable to landfilling, as it removes this hazardous waste from the environment and convert it to a useful transportation fuel and power. In **CHAPTER 19** we conducted a Techno-economic analysis, evaluates the financial viability of three processes. Waste to tire power, waste tire to methanol and power and waste tire to methane and power. This analysis will determine what is the commodity value of waste tire as an energy material and what are the highest value process pathways for chemical conversion of tires? Net present value (NPV), internal rate of return, and payback period are the economic analysis tools that will be used to determine the viability of the developed waste tire valorisation processes. The main research findings of the current study are outlined in **CHAPTER 10**.

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2 Literature Review

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Short summary

The chapter gives an analysis of the recent developments in waste tire thermochemical conversion processes with the focus on pyrolysis and gasification processes. A version of this chapter was published in the above-mentioned journal in 2020. Due to the continued developments in this area, a revised version that includes studies between 2020 and 2023 is thus presented. Substantial literature exists on the usage of pyrolysis and gasification pathways for waste tire conversion, and some of it will be reviewed in the context of evolutionary behavior, energetic feasibility, and economic analysis in order to identify the knowledge gap relative to the available studies. Waste tires fall in the category of waste that is exceedingly difficult to recycle. This review covers the effect of parameters such as catalysts, temperature and co-treatment with other feedstocks, that are used to improve the thermochemical conversion of tyres. The cost of commercialising these process pathways is also evaluated. The review also seeks to find what is the most efficient and effective way to analyse these processes using fundamental principles.

Declaration by canditate:

The scope of my contribution to the chapter are as follows:

Literature study	100%
Compilation of chapter	100%

The following co-authors have contributed to this chapter as per following:

Co-author	Nature of contribution		Contact and signture
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I declare that the above information is true and reflects the nature and extent of the contributions of the candidate and the co-authors

Signature of candidate:…………………………… Date:Athi-enkosi Mavukwana

Recent developments in waste tire pyrolysis and gasification processes

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Abstract

Waste tire generation in South Africa is one of the issues that have not found a sustainable solution. Approximately 1.5 billion tires are produced annually around the world, and South Africa contributes about 11 million tires accounting to about 250 000 tons of waste annually. Numerous technologies have been used as possible pathways to recycle waste tires. This review analyzes the main advances in waste tire pyrolysis and gasification technologies and lists challenges and successes. For waste tire pyrolysis, recovering high-value products such as limonene, benzene, xylene, and activated carbon can make the process profitable. For gasification, the objective of new studies is for the producer gas to have a desirable composition for further application in the production of chemicals, heat and power and synthesis of liquid fuels. Also, more research is required to fill the gap in the optimum conditions for solar integrated pyrolysis and gasification of waste tires. A comprehensive comparative techno-economic analysis of chemicals production from waste tire via gasification is required to determine the most commercially viable route for tires.

Keywords: Waste tires, pyrolysis, gasification, life cycle assessment (LCA), techno-economic analysis, process synthesis

2.1 Introduction

The Increasing energy demands and strict environmental pollution policies, as well as the depletion of raw materials, have put pressure on the scientific community to develop novel technologies and ideas that conserve raw materials, mitigate environmental impact, and convert low-value wastes to high-value chemicals or energy. The modern society produces a vast array of different waste materials, all of which have the potential to be processed into something of value. In 2022, the Organisation for Economic Co-operation and Development (OECD), announced that only 9% of the global plastic waste is recycled while 22% is mismanaged [1]. While most of the developed world (e.g., USA, EU, and Canada) mismanages about than 10% of their plastics waste, Africa is said to mismanage over 64% of their produced waste. Godfrey et al. [2] also revealed that nearly half of all MSW generated in Africa, remains within the cities and towns, or dumped onto sidewalks, open fields, stormwater drains and rivers. With the world population surpassing eight billion, waste generation will continue to rise, therefore, there is a need to expedite the recycling and reuse initiatives.

The South African government has identified 38 streams of waste that need to be diverted away from landfills through recycling. Waste tire generation in South Africa is one of the issues that have not found a sustainable solution yet. Globally over 1.5 billion waste tires reach the end of their useful lives every year generating approximately 17 million tons of waste tires [3–7]. Recent studies estimate the global tire production increases by 4.1%, which means by the end of 2022 almost 3.2 billion tires had been produced. Each year South Africa generates an estimated 250,000 tonnes of waste tires adding to an existing stockpile of 900,000 tonnes spread across 26 national storage depots without a robust plan for reprocessing or recycling [8,9]. The USA alone generated over 274 million scrap tires representing over 5 million tons of scrap waste tires in 2021. Europe produced 4.24 million tons of tires in 2020 [10]. The South African government has identified the issue of waste tires as a major area of environmental concern, resulting in the approval of an integrated industry waste tire management plan entitled 'Recycling and Economic Development Initiative of South Africa (REDISA)' following the National Environmental Management: Waste Act, 2008 (Act No. 59 of 2008) as stated in the Government Gazette, 17 April 2012, No.35147 [11]. However, due to mismanagement, the program failed leaving the waste tire recycling plan in tatters. A new draft waste tire management plan (IndWTMP) issued by the CSIR in 2022 indicates the combined recycling and reuse of waste tires as 20% while the rest are stockpiled [8]. This is far in comparison to

Europe where the recycling and reuse rate is more than 95% [12]. The European Tire and Rubber Manufacturers' Association (ETRMA) reports that in 2019, Europe produced 3.26 million tonnes of waste tires, and about 95% were collected and treated for material recycling and energy recovery [13]. In the United States (US), over 95% of stockpiled tires have been cleaned up by 2021 and the recycling and reuse rate is more than 71% [14]. To reduce the annual generated waste and stockpile, the waste tire processing capacity of South Africa must be expanded. The vision and mission of the IndWTMP are to achieve 80% processing/recycling capacity of the annually generated waste tire by 2035 and a 90% reduction of the current stockpile by 2038. The achieve this, the IndWTMP advises using the incentives developed by the government to create additional processing capacity by upscaling or increasing the capacity of existing processing facilities where feasible and establishing new processing capacity. In other words, the government must provide subsidies for new plant establishment, equipment upgrades, and grants on a cost-sharing basis.

Waste tires represent a petroleum waste stream with a high carbon component and have a comparatively high caloric value, making them competitive with other types of fuel, such as coal, and biomass which have much lower caloric values [15]. If all waste tires produced in South Africa are converted to energy, up to 2GWh per annum of electricity could be produced. Fossil fuels remain the major source of South Africa's energy needs with only 2% coming from alternate sources [16]. Successful conversion of waste tires to power can improve the country's energy mix and alleviate some of the dependency on expensive fossil fuels such as diesel. Alternatively, waste tires can be used to produce a vast array of chemical products through thermochemical conversion processes such as gasification, pyrolysis, liquefaction, and devulcanization ot through recycling and resues initiatives such as retreading, crumbing, artificial turfs, cement manufacturing, concrete and other civil engineering applications.

Despite this, waste tires still fall into the category of waste that is exceedingly difficult to recycle. Tires are produced from a complex mixture of synthetic and natural, metal, fabric, and additives [17]. Each ingredient has specific properties required for qualities needed for a particular grade of the tire, and this makes tires a major environmental issue, as they are non-biodegradable due to the complex chemistry of organic polymers, metals and other inorganic chemicals. The nature of the chemical structure and formulation of tires means that they possess high volatile, low ash content and a heating value much higher than that of coal and biomass which makes them a potential raw material for both energy and liquid fuels production [18].

Numerous technologies have been used as possible pathways to recycle waste tires, and these include re-treading, incineration, mechanical recycling (shredding, crumbing and reclaiming), and energy recovery through thermal decomposition [19]. Environmental concerns, high energy cost, low market value and product demand are some of the limitations for the development of current methods of recycling tires on a commercial scale. Waste management statistics reveal that almost 50% of all waste tire recovery is through energy recovery. ETRMA statistics show that 48% of waste tires were utilized for energy recovery while 52 % were for material recycling. In the US Tire-derived fuel (TDF) accounted for 41% of the utilization [20]. In South Africa, 32% of the 54,000 treated waste tires were utilized for energy recovery and 58% for material recovery [9], while the remaining 10% were reused. However, combustion provides low energy recovery efficiency and generates many different kinds of pollutants emission. Thus, sustainable remedial technologies that can convert the intrinsic chemical energy in carbon-rich materials to valuable by-products should be investigated to avoid pollutants emissions and increase energy and materials recovery. Thermal valorization via pyrolysis and gasification have been promoted as the most promising methods of converting waste tires into useful energy and other chemical products. Pyrolysis is a thermal decomposition of organic materials in the absence of oxygen at temperatures from 300ºC to about 800ºC and often at slow heating rates to decompose organic materials to the basic components of the organic chain. Useful products such as carbon-rich solid residue (char), Liquid-oil, and non-condensable hydrocarbon-rich gas mixture are primary products on pyrolysis. Pyrolysis technology has obtained great use in polymerization and polymer identification research. Techniques such as pyrolysis-gas chromatography have been developed to fingerprint and to study unknown polymeric materials. The pyrolysis process was originally developed for the thermal decomposition of carbonaceous materials to produce biofuels, solvents, and chemicals. It can be performed in two modes: i) in slow pyrolysis, materials are decomposed at low temperatures, low heating rates and long residence time to ensure complete devolution of the material and is used to maximize the production of char, whereas ii) fast pyrolysis occurs at higher temperatures and high heating rate to decompose materials at short residence time. Fast pyrolysis is often used to maximise the production of liquid products at temperatures. Gasification is an old thermochemical conversion technology developed since the 1800s that uses sub-stoichiometric air (or oxygen), steam, heat, and pressure to convert organic substances to syngas, a mixture of carbon monoxide and hydrogen. Syngas is now the most important intermediate raw material used for the production of electricity, hydrocarbons for fuels and the synthesis of ammonia, methanol and other related products [21]. Gasification occurs via three distinct steps, which are drying, pyrolysis, and oxidation. These thermal processes may take place sequentially or simultaneously, depending on the type of gasifier and operating conditions [22]. The commonly used gasification technologies are fluidised bed gasifiers (bubbling and circulating), fixed bed gasifiers (updraft and downdraft), fluidised bed gasifiers, entrained flow gasifiers and rotary kiln reactors. For each gasifier type, syngas yield and composition are influenced by steam to tire ratio, air/oxygen equivalence ratio, catalyst, temperature, pressure, tire composition and the mode of heating (indirect or direct firing) [23]. There is a substantial body of literature on the use of these pathways for waste tire conversion, and some of it will be discussed in the context of energetic feasibility to identify a potential knowledge gap to be explored that can contribute to finding a permanent solution to this waste [20].

2.2 Waste tire composition

A tire is made up of rubber mixtures, fabric, steel belt and cord. Each material has specific properties to provide the tire with the required mechanical strength and flexibility [24], [25]. The rubber mixtures and elastomers are the main components of tires. This mixture consists of natural rubber derived from the sap of the Hevea Brasiliensis tree and synthetic rubbers that are derived from petroleum-based products. Synthetic rubbers used in tires are often stirene-butadiene (SBR) and butadiene rubber (BR). SBR is a copolymer formed from stirene (25 wt.%) and 75 wt.% butadiene, its primary use in tires is for resistance to bending and wear. BR consists of repeating units of butadiene and provides the tire with mechanical properties such as rolling resistance and abrasion resistance. The rubber mixtures are strengthened with carbon black and amorphous silica, which make the tire durable and resistant to wear and tear [24,25]. Rubber in its natural form is very sticky and has poor mechanical properties and to eliminate this; tires are vulcanized via the addition of sulfur which creates cross-links (bridges) between individual polymer chains thus making the tire more durable and has improved mechanical properties like elasticity. Cross-linking binds together all the polymer chains at multiple points, producing, in principle, one giant covalently bonded molecule commonly called a polymer network characterized by non-reversible sulfur crosslinks. Zinc oxide is also added to act as an activator to speed up the process of vulcanization. Metals and fabric (nylon, rayon, and polyester) make up the structural components of tires [24,25]. The present of carbon, metals, fabric as we as the non-reversible nature of the covalently bonded cross-links makes tires difficult to recycle. Tire polymers in their natural state can dissolve in solvents; however, when cross-linked, they form a gel state that does not dissolve making recycling by solvent extraction difficult. Table 2.1 shows the common composition of passenger and truck tires. The rubber mixture of heavy-duty tires contains more natural rubber than a small car and motorcycle tires [26]. The composition is used to determine the mass balance of waste tire treatment methods. Table 2.2 shows the ultimate and proximate analysis of tires from different sources, it can be observed that a tire possesses a higher volatile matter than coal. Tires also has a heating value of 36-40MJ/kg, which is greater than that of coal averaging at about 30MJ/kg. The average carbon content of waste tires is more than 80 wt.% which is also greater than that of coal, which averages just above 60 wt.%. The moisture content and ash content of tires are less than 1wt. % and 5 wt.% compared 7 wt.% and 11 wt.% for coal. Therefore, waste tires are a highly combustible material, it is thus not surprising that there is an increase in the need to harness this energy. Sharma [27], showed that valuable products (fuel, char, chemicals and steel, etc.) can be recovered from waste tires by using novel processes such as incinerators with energy recovery systems, the pyrolysis process using electric or microwave heating, gasification to liquid fuels etc. A systematic method needs to be developed to determine which one of the many waste tire conversion technologies utilise the raw material efficiency with minimal impact on the environment and cheaper or provides higher profitability.

2.3 A brief overview of tire other recycling processes

Waste tires contain a wide range of materials which can be recovered (steel, fibres, shredders, energy, oils, carbon filer, activated carbon etc). Various processes have been developed to conserve available resources, recover useful products, combat disposal problems and minimise pollution effects. A summary of the operation of nine waste tire recovery processes is given.

2.3.1 Retreading/moulding

Retreading is one of the effective ways to extend the life of waste tires, and it's generally the most preferred solution for heavy-duty tires. Retreading is a process of replacing the tread (the layer in contact with the ground) with a new rubber layer by vulcanization [26]. The internal structures of the tire must be certified to be in a condition that it can be re-used. Truck tires are the most retreaded due to the high resistance of its internal structure, and they can be retreaded three to four times [26]. Tire retreading can be a profitable method because it uses only 30% of the energy and 25% of the raw materials required to manufacture a new one [36]. However, passenger car tires are not retreaded because of their uncompetitive price against a new tire, more reduced quality and safety when used at high speeds [37,38]. Therefore limitations of this method are the consumer attitude concerning safety and reliability, and the cost of retreaded tires versus the competition from the new tire prices [39,40]. Additionally, there is a finite number of times retreading can only be applied, these tires will eventually end up in landfill regardless.

Table 2.1. Tyre composition

	Literature sources					
Tyre composition	[28]		[24]		[26]	
Material (wt.%)	Car tyre	Truck tyre	Car tyre	Truck tyre	Car tyre	Truck tyre
rubber	47	45	45	45	41	41
carbon black	21,5	22	28	20	26	26
metal	16,5	21,5	13	25	16,5	25
Fabric	5,5	0			5,5	0
additives	7,5	5	14	10	5	5
sulfur	1	1			5	5
zinc oxide	1	2			1	

Table 2.2. Comparison of waste tire thermal properties with coal

	[29]	[30]	[31]	[32]	[33]	[34]	[35]		COAL
Ultimate Analysis wt.%									
C	83.27	73.8	77.3	81.74	75	77.3	85.5	86.3	67.69
H	7.09	6.8	6.2	7.06	7	6.2	7.46	7.37	4.59
N	0.24	0.3	0.6	0.3	0.3	0.6	0.11	0.12	1.13
O	2.17	9	7.1	2.42	2.7	7.3	5.45	4.98	5.48
S	1.83	1.3	1.8	1.82	1.5	1,8	1.48	1.23	2.3
Proximate Analysis wt.%									
Moisture	0.62	1	0	0	1.5	0	1.1	1	7.76
FC	27.96	23.2	25.5	27.04	30	25.5	39.4	37.4	47.14
VM	66.64	68	67.7	66.3	55	67.7	56.3	57	34.05
ASH	4.78	8.8	6.8	6.66	13.5	6.8	3.2	4.6	11.05
LHV (MJ/kg	36	36	-	37.1	19	33.96	42.5	41.9	30

2.3.2 Shredding and Crumbing

Currently 52% of scrap tyres are managed through shredding and crumbing [13]. Rubber, steel wire and fabric can be recovered from waste tires through a complex process involving shredding, grinding, milling as well as magnetic separation and fractionation [41]. The recovered rubber can be used to make new polymeric products. Grinding plants often involve several consecutive grinding steps to produce fine granulate or rubber powder of a proper size depending on the desired application. They are generally low-cost processes, with minimal emissions and are the primary step of managing waste tires. There are four methods of shredding that are often employed depending on the quality of crumb rubber required: conventional mechanical grinding, cryogenic grinding, wet grinding and water jet grinding. In mechanical grinding, a combination of shredders, grinding, knife granulators and mills are used repeatedly to obtain the desired crumb size. In cryogenic grinding the rubber is cooled using liquid nitrogen at a temperature ranging between - 87 and -198 °C, below the glass transition temperature of rubber [42,43]. The rubber becomes brittle, and a hummer mill breaks it down to fine powder. The main advantage of this process over the mechanical grinding is the possibility of obtaining very fine powder (up to one hundred microns) [27]. The crumb rubber produced by the processes differs in surface characteristics owing to the differences in operating procedures [42].

In wet grinding shredded tire are mixed with water to form a rubber granulate suspension which is ground using stationary and moving grindstones. The water present in the rubber granulate suspension helps to cool the grindstones used as well as the products formed. Water jet grinding is used high resistant large sized tractor tires. This process utilises high pressure (above 2000bar) and high velocity to shred tire to narrow strips. The method is used to avoid large sized grinding machines which would consume an excessive amount of energy [26,44].

The crumb rubber recovered from grinding also has many applications in civil engineering applications such as:

- Modifiers in asphalt [43,45],
- Additives in Portland cement concrete [46]
- Lightweight fillers

- Also used as a fuel for thermolysis and reclaiming processes [47].

The major disadvantage of crumb rubber industry is the low market demand, coupled with the high energy intensity of grinding processes. However, waste management regulations in many countries prefer this option as it produces fewer carbon emissions.

2.3.3 Reclaiming rubber

Devulcanization is the process used to selectively break the carbon bonds of long-chain polymers as well as the sulfur cross-links, reducing the three-dimensional strong thermoset polymers into two-dimensional thermoplastic products [48–50]. The reclaimed rubber has uses in polymeric blends and the amount of recycled rubber mixed in new rubber products can be increased without compromising their mechanical properties [26]. Conventional methods used for devulcanization of tire rubber are thermomechanical, thermochemical, mechanochemical, and microwave, ultrasound, chemolithotroph bacteria, and supercritical carbon dioxide [48,51]. Thermochemical devulcanization methods are still the most used methods due to the reclaimed rubber retaining most of the mechanical properties as compared to other methods. Solvents such as organic disulfides and mercaptans, rosin are used in combination with thermal treatment to reclaim rubber. However, many of the solvents used are polluting and thus thermochemical desulfurization are gradually being replaced with greener options such as the thermomechanical and mechanochemical and microwave treatments. Since the energy needed to break the C–C bond is slightly higher compared to C–S and S–S bonds, it is theoretically possible to send the exact amount of energy needed for the sulfur bonds scission versus main chain degradation [49]. Thermomechanical makes us of extrusion to deliver the appropriate heat transfer, shear force to plasticize rubber [52]. Whereas microwave treatment, microwave irradiation precisely control the amount of energy delivered to the waste rubber (microwave irradiation) to selectively cause the sulfur bonds scission versus main C-C bonds [48,49]. Devulcanization industry is dominant in China where to date there are approximately 500 facilities of which over 50 of these facilities can process more than 1 million tonnes per year [53]. The reclaimed rubber monomers are used as additives in the production of new rubber mixtures. The only disadvantage is that the reclaimed rubber mechanical properties are very poor compared to the virgin rubber.

2.3.4 Asphalt Pavement

In 1995 the United States of America put to law the Intermodal Surface Transportation Efficiency Act of 1991 (ISTEA), Public Law 102-240, mandating all states to use tire modified asphalt to pave approximately 5% of their annual federally funded roads or paved surfaces. In 1998, almost 20% of all paving projects funded by the federal government were paved using rubber-modified asphalt [54]. This law was enacted after a thorough review which resolved that crumb rubber would improve the asphalt film thickness, binder resiliency, viscosity, and shear strength [42]. Crumb rubber increases asphalt pavements resistance to fatigue cracking, rutting, and low-temperature cracking, decreased traffic noise, and can perform better than conventional gravel on asphalt pavements [55]. It has been shown that the adhesion of the vehicle wheels to the surface of the rubber modified asphalt is improved compared to unmodified asphalt [56]. Although inclusion of rubber into asphalt has been successful it still suffers from poor compatibility [56–58]. The mixture of crumb rubber and asphalt mix is considered a thermodynamically unstable system since rubber is chemically inert to form strong interfacial interaction and adhesion with asphalt matrix. Additionally, the vulcanized three-dimensional crosslinking polymer network inside the rubber prevents asphalt components from penetrating into the bulk of rubber and interacting with one another [55,56,58,59]. Therefore, rubberized has a propensity to separate when exposed to high temperatures during static storage or when being transported to the paving site [58]. Adding solvents to the rubberised asphalt mix as wells de-crosslinking the rubber has been used to improve compatibility and stability. De-crosslinking rubber comes with added extra cost. Therefore, further research is still required since the cost of crumb rubber modified pavements are higher than the conventional methods. Rubber modified asphalt is estimated to be about one and half that of unmodified asphalts [56].

2.3.5 Concrete

In recent years research has moved to investigate the use of waste tires in the concrete industry. The concrete industry consumes large amounts of natural resources and concrete now forms the basis of all construction projects around the world [54,60,61]. Adding crumb rubber in concrete has been shown to improve properties such as increased hardness and ductility, resistance to cracks, resistance to freezing, thawing and acid attack [55,62,63]. Crumb also improves the damping ratio of the concrete. Also concrete is made more ecological and cost-effective by incorporating recycled waste components [64]. Therefore, there is a great potential to use waste tire rubber as a partial substitute for aggregate in cement concrete. However, owing to two technical factors mainly; (1) the incompatibility issues caused by the chemical composition and stiffness, (2) the use of recycled waste tires has not been successful in concrete as well as in asphalt. It was found that replacing the conventional aggregate with rubber reduces the compressive strength, flexural strength, splitting tensile strength and modulus elasticity [46,63,65]. Concrete with about 40% of rubber content can have reduced physical properties by up to 60%. Therefore, there is a limit to how much tires. Recycled rubber is typically used to replace natural aggregates (fine and coarse fractions) up to a maximum of 40% [66]. A study [67] by revealed that using 5%, 12.5 %, and 20% waste tires results in a 15%, 50%, and 70% reduction in compressive strength, respectively, when compared to traditional concrete. In [68] was discovered that the addition of rubber particles in concrete block reduced the strength by 56%. The problem is that rubber is hydrophobic (creates a weak interfacial bond between the rubber and cement mortar) and has very low modulus which affects the stiffness of the concrete [42]. The incorporation of steel fibres extracted from waste tires into rubberised concrete appears to be a potentially profitable engineering application, increasing compressive and flexural strength by more than 10% and 50%, respectively [64,69]. However, extracting just steel fibres from tire still comes with the problem off where the rest of the waste tire components should go. A fully integrated system that consumes the entire waste tire is required. Therefore, there are research opportunities in this area to develop usable rubber-modified concrete.

2.3.6 Incineration

The burning of waste tyre in steam-generating incinerates or as supplementary fuel is a proven waste disposal option [12,44,70]. Global waste tyre management plans suggest that close to half of scrap tires are reused as tire derived fuel in incineration and cement manufacturing. ETRMA statistics show that 48% of waste tires were utilized for energy recovery. In the US Tire-derived fuel (TDF) accounted for 41% of the utilization. In South Africa, 32% were utilized for energy recovery and 58% for material recovery. In the developed world less than 20% of tire derived fuel is reused in incineration process [14,20]. Incineration is the destruction of organic material to inert residue by application of heat in a high-temperature controlled combustion chamber. The heat produced is used to generate steam for industrial processes or electricity generation. The process is self-sustaining. Below are the advantages and limitations of the process [37] [70].

The advantages of incineration are:

1. The volume and weight of the tire is reduced by over 90%.
2. Reduction is immediate.
3. Net energy production.
4. Reduced power-production costs.
5. Destruction of organic material which is harmful to human health.
6. Environmentally acceptable process.
7. Low air-pollution emissions compared to traditional fuels.

The limitations of waste tires incineration are:

1. Production of ash: Lead, and cadmium salts used as stabilisers during tire production remain as ash causing disposal problems.
2. Release of toxic gases such as SO_2, H_2S, HCl, HCN requires further treatment.
3. Production of soot. Tires have a much higher heating value than most fuels thus require further combustion higher flame temperatures since incomplete burning of waste tires produces soot.
4. Appropriate incinerators have to be designed for excellent burning and reduced soot production.
5. Requires Large capital-investment and skilled labour is required to operate the system leading to relatively high operating cost.

2.3.7 Portland Cement

Almost 50% of waste tires for fuel are consumed by the cement industry, wherein they are used as a substitute fuel for coal. Approximately 90% of Cement kilns were traditional fuelled by coal. Cement manufacturing is a highly energy-intensive process which involves roasting of a pulverized mixture of limestone, clay, or shale, iron ore or iron waste in a rotary kiln at temperatures around 1650°C to produce partially fused nodules called clinker. The clinker is then pulverized to a powder and mixed with gypsum to make cement. The higher temperatures and longer residence time of gases, high turbulence in a cement kiln ensure the complete combustion of organic matter, and this would favour the waste tire transformation [71]. The ash residue formed from waste tire combustion becomes part of the chemistry of the cement, the iron contained in the tire steel beads and belts is consumed in the process without changing the cement quality [72,73]. This reduces the additive required, such as iron oxide. Therefore, the use of waste tires could help reduce the costs of cement production.

2.4 Life cycle assessment (LCA) of waste tire recovery processes

Life cycle assessment (LCA) approach is a very useful tool to identify concerning environmental emissions and net benefits and economic points of view, which the processes or technology is the best to utilise a raw material or waste material. LCA is drawn from a series of international standards, in particular, the ISO 14040-14043, issued in 1997 [47,74].

According to ISO 14040, the LCA methodology is divided into three steps:

1. Goal and scope definition:
    a. Defining the study purpose and its scope
    b. The product unit of analysis (functional unit)
    c. Draw the system boundary indicating (raw material and energy) inputs and emissions and waste outputs.
2. Inventory analysis
    a. The inventory analysis is a quantitate description of all flows of materials and energy across the system boundary either into or out of the system.
3. Impact assessment
    a. Identifies which environmental impact to analyse.

b. examines the mass and energy inventory input and output data for a product system to translate these data to identify their possible environmental relevance and significance better.

Waste tires have a high energy content which is available for use in its thermal form. Since waste tire are obtained from the environment, it is necessary to determine to whom this consumption should be allocated [75]. The environmental assessment of each of these methods used for waste tire recycling was evaluated, taking into account both the direct impacts associated with the recovery method and the impacts avoided through the substitution effect [75].

Authors [47,76–78], conducted a Life cycle assessment of various waste recovery processes. Their analysis showed that from the total energy and raw material balance, waste tire combustion or substitution in cement production and its use in waste-to-energy processes (incineration) was more advantageous than the other means of managing rubber wastes from an environmental, technical and economical point of view. The worst performing was the cryogenic and mechanical pulverisation for reuse as filling materials, because of the high energy consumption related to pulverisation processes. Results from [76,77] also indicated that beneficial reuse of waste tires, particularly in artificial turf, create opportunities to reduce greenhouse gas (GHG) emissions, air toxins, and water consumption. However, the market for artificial turf is saturated, thus limiting its potential for large-scale utilization. Table 2.3 shows the equivalent kg CO_2 emissions per ton of waste tires for different technologies studied. Energy recovery processes and artificial turf provides, in most cases a significant environmental benefit compared to other technologies concerning emissions savings.

Table 2.3: Environmental impact of waste tyre recovery processes in kg CO_2 per ton waste tyre (equivalent) [79].

Reference	Technology	Kg CO_2/ton tyre
[80]	Retreading	1240
	Incineration	-1110
	Steel works	-142
	Asphalt	662
	Artificial turf	-1320
[77]	Retreading	-19
	Incineration	-400
	Cement	-543
	Artificial turf	-1900
	Asphalt	500
	Combustion	
[47]	Mechanical pulverisation	122
	Cryogenic	455
	Waste to energy	-870
	Cement	1
[76]	Synthetic turf	-3217
	Cement works	-1466
	Energy for urban heating	-1275
	foundries	-1193
	moulded objects	-2701
	Steel works	-672

Silvestraviciute and Karaliunaite [78], found that the co-incineration process in a cement kiln recovers approximately 2 times more energy compared to the energetic value of combustible products of thermolysis, and the process produces practically no solid waste. All the ash and slag became part of the clinker. Waste tire fuelled process produced a few greenhouse gases compared to coal only process. For every ton of waste tire used in the cement kiln replacing coal approximately 543 kg of CO_2 emissions are avoided. This increases to 613 CO_2 kg eq. per metric ton if it is considered that a fraction of tires (Natural rubber) is derived from biomass and its emissions can thus be deductible.

In studies conducted by [27,53], pyrolysis was shown the least impact on the environment and achieved a higher energy recovery than incineration and devulcanization processes. This puts pyrolysis as the lead technology for energy, as well as the production of useful chemicals from tires. However, despite having the highest net-benefit and least environmental impacts, its commercialization is restricted by the quality of carbon black and the price of pyrolysis oil.

Therefore, further research on the improvement of pyrolysis products is required to satisfy the economic conditions set by the world market. However, regardless of the recovery method studied, and regardless of the impact being studied, recycling or management of waste tires is better than landfilling or illegally disposing of them in open fields (Clauzade and Osset, 2010).

The above LCA analysis did not consider the chemical potential efficiency or exergy efficiency of the processes. Chemical potential efficiency is a parameter that quantifies how much of the chemical potential stored in tires has been transferred to the desired products [81,82]. The exergy analysis is the measure of useful energy of a system, which is the maximum work that a system can release. Only a reversible process can achieve this work potential. A system in equilibrium with the environment has zero exergies as the system deviates from the environment the exergy of that system increases. Exergy efficiency is a measure of system reversibility or idealist. Therefore, exergy analysis is the appropriate parameter for the depletion of natural resources, addressing the life cycle irreversibility.

Exergy life cycle assessment (ELCA) is simply an extension to the already established LCA. This extension was developed by Cornelissen, 1997 by combining the life cycle approach with exergy analysis. An LCA inclusive of thermodynamic perfections of the system allows the assessment of energy and material flows interaction outside the system's boundaries. In this way, the thermodynamic perfection of the production process is evaluated by the irreversibility of the complete life cycle.

The goal definition and scoping of the LCA and ELCA are identical, but the inventory analysis of the ELCA is more extensive. The impact assessment in ELCA is restricted to calculation of the exergy flows and exergy destruction in a process [47]. The cumulation of all exergy destruction in the life cycle gives the life cycle irreversibility of the product. The minimisation of the life cycle irreversibility is the target and is used as the improvement analysis. The results from [47], showed that cryogenic crumbing has the highest exergy destruction, followed by the fuel substitution and mechanical grinding processes. The waste-to-energy processes were shown to perform better since they achieved a negative value of the exergy destruction indicator, hence to exergy saving.

From both the LCA and ELCA analysis, waste tire to energy processes prove to be the optimum route to utilise tires from both thermodynamic and environmental point of view. Data from all waste management report show that tire derived fuel is responsible for over 50% of recycling options [83]. In countries such as Poland, combustion of tires in the cement works accounts for

70% of the disposal of waste tires. However, [83], argued that if the energy invested in the production of a tire is considered, then based on the energy balance point of view, only 37% (32MJ/kg) of the total energy (86MJ/kg) that is required to manufacture new rubber tire is recovered as energy. Which means it is preferable to reduce the amount of rubber produced from raw materials and to replace them with composite materials with similar specifications containing products obtained from tire recycling [44].

2.5 Recent developments on pyrolysis and gasification of tires

2.5.1 Waste tire pyrolysis

Review studies by [3,25,84–86] reveal the potential of pyrolysis as a waste management process for tires. When tires are pyrolyzed, they produce three products that can be used as fuel or chemicals in many industrial applications. The decomposition of tires under inert conditions produces 5-20 wt.% gas, 40-60 wt.% liquid, and 30-40 wt.% solids. The yield of each phase depends on the operating conditions such as temperature, heating rate, residence time and tire composition. The liquid phase mainly called the tire-derived-oil (TDO)/tire pyrolytic oil (TPO) is a complex mixture of aromatic hydrocarbons, n-paraffin and olefins terpenes, mono and poly aromatics, nitrogen and sulfur containing heterocycles and oxygenates [37,87]. The oil can be upgraded and sold as fuel. The solid fraction called char is a mixture of carbon black and other inorganic substances such as zinc, sulfur, silica, and clay. The gas phase is mostly a mixture of non-condensable light hydrocarbons (C1-C5), hydrogen, CO_x, and sulfur compounds (SO_x and H_2S), this gas product is generally used as fuel gas to heat the pyrolysis furnace [88]. Table 2.4 provides a summary of the major products produced from pyrolysis of tires. There are many studies done on the environmental benefits of waste tire pyrolysis, and all focused on the energy recovery from the pyrolytic products. In [89] it was discovered that the pyrolysis process performed better thermodynamically than the gasification route, with a higher overall carbon efficiency and chemical potential efficiency, implying that the pyrolysis process conserves the carbon resource and has a low environmental impact. Despite these concentrated efforts, it is reported that companies involved in waste tire pyrolysis are closing due to difficulty in finding a market for the liquid and solid products because of their poor quality [90].

The studies on waste tire pyrolysis effectively evaluated the noteworthy effects of temperature, heating rate, catalyst, and reactor configurations on the products and conversion rate. The conclusion drawn from these studies was that there are no recommendable pyrolysis conditions as they vary from author to author. This makes it difficult for industrial applications. Another limitation with pyrolysis is the challenge to distribute the heat evenly and efficiently such that the temperature is evenly distributed within the reactor. Poor temperature distribution affects the decomposition and cracking reactions necessary to achieve quality products. The major drawback with pyrolysis is the poor quality of the products. The char produced is a heterogeneous material with high ash content, with poor particle size, absorption properties, structure, surface chemistry and activity which means it cannot be sold as carbon black or activated carbon and this affects the economic feasibility of tires. On the other hand, the oil produced is composed mostly of heavy cyclic olefins, not attractive enough to be sold as high-value fuel. However, much of current research is focused on the production of activated carbon and carbon black, and the upgrading of pyrolysis oil as well as maximizing the limonene concentration in the pyrolysis oil to improve the industrial viability of waste tire pyrolysis.

An early study by Frigo et al [93], investigated the optimal conditions to produce pyrolysis oil from waste tires and its application in a diesel engine. These authors used an innovative pilot-scale twin screw extruder set up as a thermo-mechanic cracking reactor with two heating zones, the highest set at 500°C. In this set up the maximum product, the yield was found to be 45 wt% oil, 50 wt% char and 5 wt% gas. The pyrolysis oil showed properties comparable to petroleum diesel fuel. However, the sulphur content of tire pyrolysis oil was significantly higher and the ignition index lower than that commercial diesel fuel. Engine tests showed that a blend of up to 20% pyrolytic oil and 80% commercial diesel can be applied directly in diesel engines without engine modifications. However, modifications of the injection unit are necessary for blends using 20%-40% pyrolytic oil to compensate for the longer ignition delay. Blends exceeding 40% pyrolytic oil were not recommended. Therefore, the high sulphur content in tire pyrolysis oil limits its use to only stationary and marine engines.

Table 2.4: Major products of tire pyrolysis [91,92]

Product	Source
Toluene Styrene Benzene Ethylbenzene Paraffin C5-C9 o-Xylene m-Xylene p-Xylene	SBR
4-Vynil-cyclohexene Cyclohexane Cyclopentene Cycloheptadiene Butadiene	BR
1-Pentene 1-Hexene 2 Methyl-1-pentene 2 Methyl-1-butene 2 Methyl-1-hexene 2-Methyl-1,3-butadiene Limonene	NR
CO_x Sulphur dioxide Hydrogen Sulphide Pentene, isoprene Butane and Butenes Propane, propylene Ethane, ethenes Methane Hydrogen Char	Non-condensable gases and Char

Hita et al [37], explored the challenges of the liquid product of pyrolysis. The barriers preventing the direct application of pyrolysis oil were summarized as follows; (1) contain a very high sulphur content, (2) high content of aromatic hydrocarbons, and (iii) great proportion of molecules with similar boiling point range (BP of 350 °C). Literature studies attribute most of the inferior properties in pyrolysis oil to the sulfur, nitrogen, and oxygen-containing polar compounds present in it. Which means waste tire pyrolysis oil requires major upgrading before use. Recent, studies on pyrolysis are dedicated on investigating methods of upgrading the oil both during pyrolysis and as additional treatment steps. The method used for upgrading the pyrolysis oil are hydrocracking (HC), hydrodesulfurization (HDS), and hydrodearomatization (HAD). High pressure, high temperature and catalysts are employed upgrade tire pyrolysis oil to commercial state. Karagöz et al [5], developed a four-step process to improve the quality of pyrolysis oil. Step one is acid washing wherein the pyrolysis oil from a reactor is mixed with sulphuric acid at a ratio of 12:1 oil to acid. After filtration, the oil from step one is de-sludged in an activated clay-calcium oxide process. From which the oil is then distilled under vacuum conditions to produce fuel with diesel-like properties. After distillation, the fuel is subjected to an oxidative desulfurization process to reduce the sulfur content of the fuel. Another research includes hydrothermal catalytic upgrading of oil using (1) formic acid as diluent and Palladium nanoparticles immobilized on the surface of magnetic alumina ($Pd/Al_2O_3/Fe_3O_4$) as catalyst [94], or (2) silica gel as adsorbent and petroleum ether as diluent [87], (3) using catalyst such as $CoMo/Al_2O_3$, $NiMo/SiO_2$-Al_2O_3 and NiW/USY zeolite [95]. The upgrading pyrolysis products does not fall on the scope of this review.

2.5.2 Waste tire pyrolysis reactors

The work conducted by [96,97] has shown that waste tire pyrolysis occurs at temperatures between 300-800°C, with 425-550 being the optimum temperature to obtain the maximum liquid/pyrolysis oil. Earlier studies by [128–132] also investigated the use of zeolite catalyst family in two-stage/ phase pyrolysis. The results of these studies have shown that the zeolite catalyst family selectively increases the hydrogenation reaction and cracking of higher hydrocarbons which increases the formation of lighter aromatic hydrocarbons, however, the cracking activity also leads to decreased oil yields while increasing the gas productivity [86]. The Y-zeolites catalyst outperformed the HZSM-5 zeolite owing to higher pore size, however, lead to coke formation [127]. Ding et al [133], using a Pyrolyzer- Gas Chromatograph/Mass Spectrum (Py-GC/MS) reactor showed that the HY zeolite catalyst showed better aromatization ability compared to the HZ catalyst, however, the HZ catalyst showed better selectivity to smaller compounds such as BTXE (benzene, toluene, xylene and ethylbenzene) than HY catalyst. However, from all these studies it can be concluded that diesel fraction with lighter/smaller aromatic compounds can be achieved using the zeolites catalyst with controlled acidity [127]. This provides the first step towards producing a clean oil from tires.

Table 2.5 shows the distribution of the pyrolysis products with temperature, from the table, it is clear that an increase in temperature favours the secondary decomposition reactions leading to increased gas production. Besides temperature, the product distribution in waste tire pyrolysis is largely affected by the reactor type and configuration. The rate at which heat is transferred as well as the reactor residence time influences the quality of the liquid oil and gas composition. It was mentioned earlier that the pyrolysis process can be categorised according to slow and fast pyrolysis. Pyrolysis reactors are thus grouped according to these categories. Fixed bed, both batch and semi-batch reactors, rotary ovens, auger reactors and stirred tank reactors, are associated with slow pyrolysis as these reactors are often operated at low temperatures and low heating rates and long residence time for both solid and vapour products formed. Fast pyrolysis reactors are fluidised bed reactors (bubbling and circulating), rotary kilns, spouted reactors and ablative reactors. These reactors perform the pyrolysis process with very short residence time and temperatures up to 600-800°C.

Taleb et al [98], used a fixed bed reactor to study the thermal behaviour of pyrolysis products. Their results concluded that the optimized liquid oil yield of 32% is achieved at 500°C, and the liquid product consists of high contents aromatic compounds such as benzene, toluene, xylene, and limonene, as well and a complex mixture of C5- C16 organic compounds. Al-Salem [99] also used a fixed bed reactor and achieved a maximum liquid yield of 48% at 500°C. These authors use a much lower inert gas flow of 20ml/min than the 5l/min used by [98], this may have contributed to the difference is the product yield since a lower inert gas flow may allow enough time for the larger gas compounds to condense.

A study by [100], showed that when using a rotary reactor the maximum yield of liquid oil was 44 wt% at the pyrolysis temperature of 550°C. The high heating value of this liquid was 39.3 MJ/kg with a specific gravity of 0.95. When the authors analysed the liquid oil, they found that it contained about 14% light naphtha, 4% heavy naphtha, and 36% middle distillate, respectively. The other 46% was a liquid with a boiling point above 350°C. A further FTIR analysis revealed that the liquid contained undesired compounds with sulphur and nitrogen functionalities, which may suggest that the liquid oil is not suitable for direct application as a diesel fuel without further purification. Bowles et al [101] also used a rotary kiln reactor and found that the maximum oil yield of 38.4 ± 0.9% at 550 ◦C. This oil contained 4.5 ± 0.1 wt% of limonene. Muelas et al [102] studied the combustion behaviour of pyrolysis oil obtained from a continuous auger reactor using a drop tube facility. The behaviour of the pyrolysis oil was compared to conventional heating oil. The pyrolysis oil was found to have considerably lower burning rates, smaller flames and a higher propensity to soot. When the pyrolysis oil was blended with heating oil, it showed considerable similarities to the pure heating oil, however, the tire pyrolysis oil-heating oil blends were limited only to 5% of tire pyrolysis oil due to its high sulfur content.

Mkhize *et al* [103], examined the effect of reactor configuration and various condenser systems on the tire pyrolysis oil, DL-limonene yield, and benzothiazole concentration in the oil. Three reactor types were investigated: a fixed bed reactor (FBR), a bubbling fluidised bed reactor (BFBR) and a conical spouted bed reactor (CSBR). Two condensation systems, a shell and tube and a quenching condenser type configuration were compared in terms of their retention efficiency, selectively as well as reduction of heteroaromatic species. The authors found a bubbling fluidised bed reactor (BFBR) and a quenching condenser are favourites to produce a high yield of oil and high yield of limonene. A study by Danon *et al* [90], showed that up to 2.5 wt% tire derived fuel (crumb) can be converted to limonene, a solvent with wide applications in cosmetics, resin and polymer industries. However, the recovery of highly pure limonene from the pyrolysis oil is still a challenge since dipentene has similar properties to 1,2,3-trimethyl benzene, m- and p-cymene and indane, also present in the pyrolysis oil. Sophisticated separation systems are required to obtained dipentene with purities between 92 and 95 wt%. However, with the price of 2 US$ per kg, limonene is a very promising route to add value to the tire pyrolysis process.

2.5.3 Catalytic pyrolysis

Other research has made use of catalysts to improve the waste tire pyrolysis products during the pyrolysis reaction process. The main application of catalyst in waste tire pyrolysis is to reduce the product distribution as compared to thermal pyrolysis and thus increase the yield of a specific selected product. If a selected catalyst provides a higher yield of gas compounds, the yields of the oil and char are often reduced over those catalysts and vice-versa [86].

Khalil et al [127], investigate d the performance of microporous zeolite catalysts compared to mesoporous MCM-41 catalyst for pyrolysis of scrap tires in a two-stage fixed bed reactor. Their result showed that the zeolite catalyst increased the production of aromatic compounds by up to 23.7% as compared to 18.7% achieved by the MCM-41 catalyst. Earlier studies by [128–132] also investigated the use of zeolite catalyst family in two-stage/ phase pyrolysis. The results of these studies have shown that the zeolite catalyst family selectively increases the hydrogenation reaction and cracking of higher hydrocarbons which increases the formation of lighter aromatic hydrocarbons, however, the cracking activity also leads to decreased oil yields while increasing the gas productivity [86]. The Y-zeolites catalyst outperformed the HZSM-5 zeolite owing to higher pore size, however, lead to coke formation [127]. Ding et al [133], using a Pyrolyzer- Gas Chromatograph/Mass Spectrum (Py-GC/MS) reactor showed that the HY zeolite catalyst showed better aromatization ability compared to the HZ catalyst, however, the HZ catalyst showed better selectivity to smaller compounds such as BTXE (benzene, toluene, xylene and ethylbenzene) than HY catalyst. However, from all these studies it can be concluded that diesel fraction with lighter/smaller aromatic compounds can be achieved using the zeolites catalyst with controlled acidity [127]. This provides the first step towards producing a clean oil from tires.

Table 2.5. Literature data on waste tire pyrolysis reactors

Literature data on fixed bed reactors

Reference	Temperature °C	Gas wt.%	Liquid Wt.%	Solid Wt.%	comment
[98]	500	26	32	42	5l/min
[99]	500	8	48	44	three heating elements
[107]	500	24	40	36	catalytic
[108]	350	3,1	53,2	43,7	
	400	11,2	62,8	26	
	450	17,3	57,2	25,5	
[109]	400	27,2	38,8	34	
[110]	550	28	42	30	non-catalytic/solar
[111]	500	13,8	48,5	37,7	
	475	17	53	35	material sizes effect
[112]	800	7,24	54,78	37,86	power
	800	18,05	3,18	37,88	bgger size (25)
[113]	600	14,3	38,6	43,3	catalytic two stage
[114]	700	30,6	33,1	44,5	two-stage
	900	56,8	19,5	39,6	
[115]	498	12	45	43	
	574	18,5	40,5	41	
Literature data on fluidized bed reactors					
[116]	**475**	**14.6**	**50**	**35.4**	
[117]	475	8.7	55.9	35.4	Quenching condenser
	475	24,9	40,6	34,5	
	550	30,2	29,3	40,5	
	600	46	25,3	28,7	
[118]	497	7,5	51,2	38,3	product gas fluidised
	614	19	41	36,5	product gas fluidised
	617	11,2	49,1	36,8	nitrogen fluidized

Table 2.5 continues…

Literature data on conical spouted bed reactors					
[119,120]	425	3,6	58,5	37,9	
	475	5,7	58,4	35,9	
	575	10,2	53,9	35,9	
[121,122]	425	1,9	64,3	33,9	
	500	4,1	62	33,9	
	600	10,1	56	33,9	
	425	1,9	64,4	34	vacuum
	500	4,3	62,4	34,4	vacuum
Literature data on rotatory reactors					
[123]	300	14	29	57	
	550	20.8	42.95	36.25	
[100]	550	21.3	44	34.7	
[124]	450	10,95	51,61	33,05	
	500	7,92	51,78	33,66	
	550	12,11	51,83	35,5	
	600	7,39	51,14	32,92	
[125]	950	33	19	48	
	850	32	20	48	
[126]	850	31	28	41	variable sizes
	850	37	34	29	

Zhang et al. [69], investigated the possibility to increase the production of hydrogen and carbon nanotubes using metal-based catalysts such as Co/Al_2O_3, Cu/Al_2O_3, Fe/Al_2O_3, and Ni/Al_2O_3 catalyst. Their results showed that Ni/Al_2O_3 catalyst produced the highest gas yield and the highest H_2 production and also produced the highest quality carbon nanotubes. Li *et al.*, 2019, also studied the effect of different catalysts namely nickel, iron, and cobalt supported on g-Al_2O_3 and activated carbon on the production of hydrogen and carbon nanotubes through pyrolysis of waste tires. Their findings showed that Nickel supported on activated carbon produced the highest H_2 yield and the best carbon nanotubes quality. This makes activated carbon a perfect, and inexpensive catalyst support to produce H_2 and carbon nanotubes. Thus, waste tire pyrolysis is the perfect technology to produce carbon nanotubes. Zhaoying Li et al [136,137] also found that Ni/ZSM-5 catalyst exerts better catalytic effects, leading to higher contents of produced H_2 and hydrocarbons. The study revealed that with the incorporation of 10 wt% Ni/ ZSM-5 catalyst, the relative content of H_2 from the catalytic pyrolysis of waste tires can be significantly improved by about 41.3 % in comparison to the same measurement done in the absence of the catalyst. Yu et al. [138] investigated the influence of Fe_2O_3 catalysts on the evolution mechanism of gas products from catalytic pyrolysis of tire rubber. The presence of Fe_2O_3 increased the proportion of CH_4 and H_2, while it reduced the proportion of

$CH_2=CH_2$. Alsurakji et al. [139] demonstrated that the synergistic effect of NiO and MgO nanoparticles (SBNs) during catalytic pyrolysis of waste tires was extremely effective in lowering the operating temperature and speeding up the pyrolysis reaction. In Kordoghli et al.[140] powdered catalyst (MgO and $CaCO_3$), acid (zeolite ZSM-5) and neutral (Al_2O_3) catalysts were investigated to determine their influence on the composition of the pyrolysis gases. The authors discovered that Al_2O_3/OS increases the gas fraction as well as the amount of gel deposited on the catalytic bed. MgO/OS had the highest concentrations of hydrogen and hydrocarbon species, to the detriment of the gas fraction. Due to the low temperature, $CaCO_3$/OS and ZSM-5/OS only achieved modest results. Biomass ashes was also found to provide significant catalytic effect than fly ash during CO_2 gasification of tire char [141]. Steel slag (SS) was used as a catalyst in catalytic pyrolysis of waste tires in CO_2 atmosphere by Cho et al. [142]. At low temperatures, the effectiveness of CO_2 on pyrolysis of waste tires was increased by nearly 400% in the presence of SS. In a another study by [143], they found that MgO based catalytic bed supported by a layer of oyster shells increased the yield of gas and H_2 production was also significantly increased from 14 to 32 vol%. In an earlier study, [144], showed that the sulphur content of the pyrolytic oil can be reduced if $Ca(OH)_2$ is used as a catalyst during pyrolysis. They succeeded in reducing the sulphur content of the oil by a total amount of 34%. The authors postulated that desulfurization reactions proceed to form CaS (Calcium Sulfide) which would leave the reactor with the solid product. No further characterisation of the solid product was done as the intention of the paper was to produce a diesel-like oil. This study also concurred with Frigo et al [93], that the 5-35% blends of pyrolysis oil can efficiently be used in diesel engines without any engine modifications. However, blends exceeding 50% produced considerably high CO, HC, SO_2 and smoke emissions.

Another study by Wang *et al* [145], showed that waste tires are a perfect feedstock for large scale production of graphene with high electrical conductivity. The authors successfully synthesised a 3D cross-linked graphene from one step KOH assisted pyrolysis at 1000ºC. In this process, the organic polymer of waste tires is converted into 3D graphene by active K vapour inducing carbon atom rearrangement. However, the study was limited to laboratory scale and did not quantify the energy requirements for the process which may be the barrier for commercialisation. Martínez et al [146] showed that quality carbon black can be obtained from tires using a demineralization process with cheap and common reagents such as HCl and NaOH. Adding a demineralization step after waste tire pyrolysis can improve the economic feasibility of the process. Other acids can be used to improve the quality of carbon black, Pundlik et al [147] used hydrochloric acid (HCl) and sulphuric acid (H_2SO_4), Akyildiz et al [148] used HCl and HNO_3, [149], used HCl and high-energy electron bombardment. In all three studies, better properties of carbon black were reported.

Arabiourrutia [3] concluded their review of catalytic tire pyrolysis process with the:

- The type of catalyst (acid, basic or metallic one) and properties of catalyst (porosity, acid strength and acid sites density) have a great influence on the characteristics and/or distribution of products.
- The choice of a catalyst depends largely on the potential applications (quality) of the product required.
- Acid catalysts such as the zeolites family promote the cracking of TPO to produce valuable chemicals, such as aromatics and light olefins. However, reduce the TPO yield promoting the yield of the gaseous product.
- Base catalysts, such as MgO, Na_2CO_3 and NaOH, promote the yield of TPO.
- CaO and $Ca(OH)_2$ reduce the sulphur content of TPO

Cao et al [150] studied the influence of CaO addition on the product distribution and sulfur transformation during the pyrolysis of scap tires. Their results indicated that addition of CaO help fixed most of the evolved sulfur-containing compounds in the char. However, in the gas phase, the presence of CaO favored SO_2 production over H_2S. Also, CaO addition had a positive effect on yields of H_2 and CO at high temperatures and reduced the production of CO_2 and CH_4. Further studies are required here to truly study the effect of CaO on the gas phase, in particular the SO_2 production. Other studies can include the use of $CaSO_4$ which has a much higher oxygen content than CaO.

However, there is a disadvantage associated with the catalyst addition in a batch reactor, which provides high propensity for the formation and accumulation of coke on the catalyst surface, thus diminishing the catalyst efficiency with time and high residual leftover in the process [20,151]. Due to carbon black formation, catalysts are often unrecognizable from the solid residue formed during gasification. This limits their reusability, and also increases the cost. A cheaper alternative is thus required to make the catalytic conversion of tires possible.

The spent fluid cracking catalyst (FCC) from the petroleum industry is an excellent replacement for catalytic waste tire gasification. To increase the output of gasoline and other hydrocarbons produced from crude oil, the petroleum industry uses the FCC catalyst as a hydrocracking, hydro refining, and catalytic reforming catalyst. [152,153]. The FCC catalyst is replaced when it is degraded and constitutes the largest solid waste stream from the petroleum industry. Due to the presence of heavy metal impurities in FCC it is regarded as hazardous waste. However, the presence of metallic oxides which act as reaction catalysts elsewhere makes the FCC a favorable candidate for use in pyrolysis and gasification [153,154]. Since waste tires are made from petroleum products, the thermal cracking of tires is similar to petroleum cracking and the FCC can be used for the catalytic cracking of tar and other hydrocarbons during the gasification of waste tires. Various studies have used FCC to upgrade tire pyrolysis oil [95,155,156]. FCC has also been used for in-situ catalytic waste tire pyrolysis [157–159]. The catalytic effect of FCC during waste tire pyrolysis has been extensively studied, and it has been demonstrated that adding FCC to the bed material produces syngas with very low tar content, eliminating the need for an additional tar cracking.

2.5.4 Co-pyrolysis with biomass

The use of renewable materials and waste valorisation is critical in medicating the effects of climate change. Biomass has long been viewed as the potential resource to help reduce the dependency on fossil fuels. Thus, the thermochemical conversion of biomass with waste tires to produce alternative fuels and valuable products can provide the needed energy security, waste management as well the mitigating the climate change [160]. Several studies on the production of liquid fuels from biomass/polymer blends found that combined synergistic effects waste materials lead to increased product yields and calorific values, reduced water content in oil products, and products that are easily separated [161].

Besides the benefits of climate change mitigation, co-pyrolyzing biomass with waste tires provide much-needed improvement in the quality of waste tire pyrolysis products as well as addressed the quantity issues associated with waste tires, alleviate the issues of fluctuations in the availability of biomass. Bio-oil obtained from biomass has limited use due to its high acidity, high water content and low heating value [162]. Whereas the oil from waste tires is limited due to the high presence of sulphur compounds as well as high molecular polycyclic aromatic compounds (PAH) which render the oil unusable. Therefore, the co-pyrolysis of biomass and tires compensates for the shortcomings of biomass in fuel production while effectively alleviating the disposal of used tires along with providing a net high calorific value and low O/C of the feedstock, which can improve the quality of the products [161]. It could also provide improved methods and pathways to consume and utilize waste tire and biomass together at high conversion efficiency and better energy transformation [160].

Hossain et al. [163], investigate the co-pyrolysis of waste tires with rice husks to produce petroleum-like fuels using a fixed-bed reactor chamber. They report that a maximum oil yield of 52 wt.% with 15 wt.% gas and 33 wt.% char was achieved with a feed ratio of 50% tire and 50% rice husks, at a fixed reactor temperature of 450°C. However, this was lower than when waste tires were used alone which achieved an oil yield of 67 wt.%. Increasing the rice husks blend was reported to reduce the yield of oil as well as the energy conversion efficiency of the pyrolysis process. This we can conclude was due to the high composition of oxygen in the biomass as well as low hydrogen to carbon ratio associated with biomass. The presence of oxygen leads to secondary reactions, breaking the high molecular compounds thus promoting the yield of gas. Thus, the observation that increasing the composition of biomass in the feed reduces the efficiency and yield of the oil. These authors calculated the efficiency of the process as $\eta = \frac{total\ energy\ in\ Oil\ product}{total\ energy\ in\ the\ feed}$. Although this equation gives the overview of the process, we believe it is limited as it excludes the energy fed into the system by the LPG heating system as well as the energy lost through the flared gas and char.

Wang et al [162] investigated the synergetic effects of co-pyrolysis of biomass and waste tire on product distribution. This work showed that biomass act as an activator for waste tire pyrolysis and waste tires with hydrogen to carbon ratio of 1:1 donates hydrogen to biomass to update the bio-oil. This was observed as the hydrocarbon content in the oil increased as the blend of tires was increase, however, an optimum ratio of 6:4 biomass to the tire was achieved. Pass this value the presence of PAH increases as tire blend increases. However, Azizi et al [164] study of co-pyrolysis of microalgae, wood and waste tires using a TGA, showed the interaction between materials is inhibitive rather than synergistic in the pyrolysis of mixtures. And that tires are inhibitive to the decomposition of other materials due to their composition. Tires increased the decomposition temperature of other materials. Martínez et al [165] concurs with this study that the decomposition behaviour of biomass is disturbed with co-pyrolysis with tires. These authors [165] postulate that at 500°C radicals released during the pyrolysis of both materials coexist which leads to interactions that produce variations among the characteristics of the pyrolysis products, leading to a single-phase liquid fuel with improved properties. In all essence, the presents of tires improve the properties of bio-oil significantly which proves a synergetic effect.

Uçar and Karagöz [166] study showed that not only does the blending of pine nut shells with waste tires improve the bio-oil by reducing the content of phenols in oil but improves the properties of char especially concerning tire chars. Char obtained from waste tire pyrolysis have significant amounts of sulphur and low amounts of oxygenated sites. Blending tires with pine nut shells led to the cracking of organic sulphur compounds in chars occurred while some organic sulphur compounds were transformed into gases. this means the sulphur compounds within the fuels meets the legislated limits which render co-pyrolysis a viable way route for both these waste materials. The same improvement in char properties was observed in [165,167,168]. In Alvarez et al [168] study, char from waste tires alone contained 3.3 wt.% sulphur and 0.7% oxygen. By blending with 50% biomass and 50% tires the sulphur content reduced to 1.8wt.% and oxygenates sites increased to 5.9wt.%, making the char suitable for the production of high-quality activated carbons. Chen et al [161] showed that waste tires react with CO_2 or carbonyl groups in tobacco stalks which subsequently lowers the CO_2 production during the co-pyrolysis process. This can be true as tires contain no oxygen and thus when mixed with biomass, waste tires volatiles will interact with the CO_2 released from the carbonylation and carboxylation of biomass to form organic gases thus removing oxygen from the bio-oil and organic gases. It is postulated that the oxygen is removed with the residue (char). Studies [165,166,169,170] as well as [168] found that that decarboxylation and decarbonylation reactions are enhanced during the co-pyrolysis process. Increasing the ratio of waste tires does have a greater effect in reducing the concentration of oxygenated compounds in the gases. Khan et al.[171], showed that demineralizing the biomass before co-pyrolysis with waste tires further increased oil yield by 13% and improved the organic content of oil by 18%. However, an overall energy efficiency inclusive of the acid washing step, as well as detail techno-economic analysis, is required to determine the commercial aspects of such a process.

Wang et al [172], evaluated the impact of co-pyrolysis with pine bark on syngas and char production; Bičáková and Straka [173], investigated the synergetic effect of co-pyrolyzing with coal on syngas and hydrogen production; Hu et al [174], investigated the thermal decomposition behaviour when co-pyrolyzing with plastics while Onay and Koca [175], investigated the potential synergistic effect when co-pyrolyzing with lignite. All these studies indicated one fundamental fact that co-pyrolysis of solid waste materials with waste tires could be an environmentally friendly method for the conversion of hazardous waste into valuable products and fuels. the nature of the blend ratio of waste materials is influenced by the desired target product.

2.5.5 The efficiency of waste tire pyrolysis

The feedstock to oil energy conversion efficiency equation seen in Hossain et al [163], is often the standard performance indicator for most pyrolysis studies. The equation simply measures how much of the calorific energy contained in the raw material is transferred to the desired product. Hence, the efficiency is defined as the ratio of pyrolysis oil energy (LHV) to the total energy of the feedstock (LHV of tires). If syngas is the target product the cold gas efficiency is the standard measure of performance of the process.

When the oil is the target product, the energy efficiency of the process decreases as the temperature is increased. As the temperature increases, there is more decomposition of larger hydrocarbon chains to form gases and smaller hydrocarbons which reduces the heat value of the oil. The reverse will be obtained if the gas is the desired product. Another performance indicator is the carbon or hydrogen efficiency, which quantifies how much of the carbon/hydrogen in the feed stream ends up in the desired products. However, in both cases often the heat input is largely not included in this calculation. Laboratory scale reactors often used electric heated furnaces or reactors and the energy cost, that is the electric heat input is overlooked. From the previous sections, waste tire pyrolysis research focuses largely on the product quality improvements, wherein the yield of oil, gas, char and the quality of oil produced is the target and the performance is measured according to the deviation to the target product specifications. Wang et al. [160], measured the efficiency as the percentage of calorific content in the syngas yield per unit raw material calorific content and energy input from electricity consumption. Ismail et al [105], calculated the net power produced from a pyrolysis process by subtracting the combustion power produced from a given oil product from the power consumed for heating the feed, and the power consumed for heating the reactor as well as the electrical power required in the shredder. In both cases the net power produced, and efficiency increased with the increase in the desired product. However, both methods still excluded the other products of pyrolysis such as char. All products of waste tire pyrolysis, even though poor in standard quality, all find commercial use. Considering them as desired would have a positive impact on the overall performance of the pyrolysis process.

Researchers often omit to investigate the energy efficiency of pyrolysis processes. The answer lies in the fact that pyrolysis is a process characterised by an excess of energy. The feed, as well as all the three products produced by the process, contain enough energy to fuel the process, thus making the process maintain a self-sustainable profile [176]. Fundamental thermodynamic analysis was used by Mavukwana et al [89] to assess the performance limits of various idealized waste tire pyrolysis process pathways. The comparison was based on carbon efficiency, exergy efficiency, and chemical potential efficiency. Pyrolysis has a carbon efficiency of 94% and a chemical potential efficiency of 93%, which means that more than the energy content of the feedstock is transferred to the products, as opposed to gasification processes, which lose about 45% of the carbon feed to carbon dioxide. And this is possibly why pyrolysis is regarded as a method able to recover the maximum value from tires (materials and energy).

2.5.6 Techno-economic analysis waste tire pyrolysis

There is an extensive literature on waste tyre pyrolysis, but this research does not translate to increased industrial application. Most waste tire pyrolysis processes are reported to have closed during the most of 2020 due to non-profitability and strict environmental policies [177]. Therefore, the academic research on waste tire pyrolysis must be followed by a detailed techno-economic analysis to determine the profitability of the processes discussed. The following section addresses this new area of research concerning waste tire pyrolysis. A techno-economic assessment is a systematic framework for evaluating a process technical and financial performance [178]. The key to any process's success is to reduce capital expenditure (CAPEX) and operating expenditure (OPEX) while increasing production volume, and thus revenues. The pyrolysis of waste tyres yields three major valuable products. The gas product is used to fuel the system, making the process self-sustaining and thus relying on two products, char and oil, for profitability. However, as previously stated, these require additional treatment to prepare them for market value. This section discusses various published literature's techno-economic analysis of waste tire pyrolysis. Using the search matrix "Waste tire AND pyrolysis and techno-economic analyses," a total of 9 relevant articles were retrieved from Scopus and the Web of Science (WoS).

Bi et al [36] developed an Aspen Plus simulation model for waste pyrolysis based on a process that considers pyrolysis oil and carbon downstream processing. The model was used to investigate the techno-economic performance of different waste tire pyrolysis processes of 20, 30, 40, and 50 ten-thousand-ton waste tires per year. This study was unique in that it included both oil hydrodesulfurization and char activation. The results showed that for a low processing capacity of 20,000 tons per year, the profit is very low and the payback period is as long as 76 years, but for a processing capacity of 50,000 tons per year, the profit is good and the payback period is shortened to 3.6 years. A similar Aspen Plus pyrolysis model with pyrolysis oil distillation for limonene extraction and purification was evaluated in [179]. A carbon efficiency of 95% was achieved from the process, with 14.7% of the carbon in the feedstock converted to limonene, 49.5% converted to pyrolytic oil, 35.6% converted to char, and 4.8% converted to carbon. As an economic indicator, the study used the minimum selling price of limonene. Two economic scenarios were investigated: pricing pyrolytic oil streams based on their heating value (S1) or selling diesel fuel (S2). The pyrolysis process was found to be economically viable with the lowest selling price in both scenarios. S1 and S2 were priced at 4291 and 1505 $/tonne, respectively, compared to a market price of around 12,000 $/tonne.

In [180] The economic viability of co-pyrolysis of waste tires and wheat husk for oil production for direct use in combustion ignition engines was assessed. This study is notable for being the first to assess the feasibility of co-pyrolysis beyond synergetic interactions. However, downstream oil and char processing was not considered in the economic scenario. It was discovered that the payback period was 12 years, with the cost pyro oil of $0.39/litre. In [181], the impact of a range of feedstock ratios on the techno-economic performance of commercial rice straw (RS) and waste tire (WT) co-pyrolysis plants was investigated in depth. On the basis of feedstock ratios, the capital investment, operating cost, production cost, and selling price of pyrolytic oil were estimated for six different scenarios. Due to synergistic interactions between the two feedstocks, the optimal combination of RS and WT was discovered to be 20:80 (Plant E), which provided the highest oil output among all combinations. The estimated capital expenditure for such a facility was $19.9 million, with a favorable payback period of 6.23 years and NPV of $5.63 million.

Tsiryapkina [182], assessed the economic viability of producing limonene from used truck tires in Russia. Based on a processing capacity of 30 tons of truck tires per day, their calculations indicated a process with an NPV of $10.39 million, a payback period of 3.6 years, and an IRR of 31.5%. An earlier research [183] determined that a 30 ton per day plant capacity in South Africa would require a $4.27 million capital expenditure, with a potential investment return and gross margin of 29.79% and 34.50%, respectively. These facilities will generate 46.8 million litres per year of refined tyre-derived oil for use in diesel engines at a cost of $0.516 per litre, in addition to additional secondary value-added products for local and foreign markets. A considerably smaller facility in Gauteng, South Africa with a capacity of 3.5 tons per day was estimated to require an investment of $1.5 million, have a payback period of around 5 years, internal rate of return of 31.9%, and a life span of 15 years. It was determined that for the pyrolysis plant to be successful, further treatment processes are required to improve the process economics; additionally, a stable and sustainable product market should exist and be regulated in South Africa [177]. Other authors [184,185] discovered that a plant in Shanghai with a capacity of 25 tons of scrap tires per day required an initial expenditure of $2.5 million. In Taiwan, a comparable facility cost $3.5 million to build. Another factory in Taiwan, constructed at a cost of $3 million, can produce 30 tons per day. The cost of a larger American factory with a daily capacity of 100 tons was $4,863,000. Islam [185] estimated the production costs of three Bangladeshi waste tire pyrolysis facilities with 144, 36, and 3.6 tons/day processing capacities. Investment and fixed and variable costs were converted to unit production cost (i.e., US dollars per ton). They determined that the unit production costs for the proposed 144, 36, and 3.6 tons/day plants are $ 136/ton, $ 193/ton, and $ 321/ton, respectively, substantially lower than furnace oil pricing in Bangladesh. In comparison [184] estimates that a medium-sized pyrolysis plant capable of recycling 30–40 tons of scrap tires per day yields $222 per ton in revenue with a $22 per ton profit margin.

The majority of the covered research concentrated only on modeling the pyrolysis reactor and condenser, without taking into account the quality and upgrading of bio-oil and char. In addition, the most important economic factors, such as net present value (NPV), payback period (PBT), gross margin (GM), and internal rate of return (IRR), were neglected in a number of research[181]. The use of non-standard techniques, assumptions, and data of various quality makes it difficult to compare the values of the literature and draw logical conclusions because the majority of the covered research employed diverse methods of techno-economic assessment [178]. In addition, the analyzed studies' processing capacities are insufficient to meet the rising tidal of waste tires in each location where their plants are located. Hence, a more standardized strategy is required to fully encapsulate the profitability of waste tire pyrolysis proceses. Equally, the government and policymakers should view the pyrolysis of waste tires as a green endeavor, as it converts trash into valuable products and might be exempt from the carbon tax linked with thermochemical processes. Second, in order to attract private investors, the government and policymakers will need to implement a product selling price guarantee or a robust policy. For improved economic performance, the tipping costs associated with dumping tires or levy charge per kilogram of tire generated in certain countries should be considered revenue for pyrolysis plants [181].

Therefore, more detailed techno-economic analysis of waste tires pyrolysis process taking advantage of revenue from tipping fees and tire levy with downstream product upgrading needs to be conducted.

2.5.7 Gasification of waste tires

The mechanism of decomposition of waste tires during gasification occurs as follows; first is the primary decomposition of tires to char, heavy hydrocarbons called tar and small fractions of light hydrocarbons. This is followed by the cracking of tar to light hydrocarbons, the steam reforming of light hydrocarbons to non-condensable gases, and lastly the gasification of the solid char material to non-condensable gases [17]. The product gas is the target of gasification, and the composition of this gas includes hydrogen, carbon monoxide, methane, carbon dioxide, a small concentration of ethylene, ethane, and propylene. The yield of each product depends on the operating parameters of the gasifier. Temperatures above 787 ºC yield the highest concentration of hydrogen, followed by carbon monoxide, carbon dioxide, and methane, according to literature studies [22,31,186].

Ongen et al[187] used a fixed bed reactor to study the gasification of waste tires in an air and oxygen atmospheres. The highest yield of syngas (41 wt%) was obtained at a gasification temperature of 800ºC under air atmosphere. When gasification was combined with the pyrolysis step, the syngas yield improved to 42.6 wt%. Under these conditions, the syngas contains 40 v/v% methane and 34 v/v% hydrogen with a high heating value of 20.5 MJ/m^3. Karatas et al [188] compared a fixed bed gasifier to a bubbling fluidized gasifier. Their study showed that the fluidised bed gasifier achieved a higher gas yield, gas LHV and syngas efficiency when compared to a fixed bed gasifier. Their study also investigated the effect of equivalence ratio (ER) and temperature on syngas product. The study showed that lower ER values result in lower concentrations of CO_2, higher concentrations of H_2 and CH_4 and higher LHVs. However, lower ER's increased the formation of polyaromatic hydrocarbons and reduced the bed temperature. ER between 0.29-0.60 are therefore recommended to keep the bed temperature above 700ºC. The LHV of the product gas ranges from 2.66-7.03 MJ/Nm^3 in this ER range, decreasing with an increase in ER. Zang et al. [32] achieved a similar LHV of 2.8-7.4 MJ/Nm^3 when ER was varied from 0.22 to 0.55 in a fluidized gasifier. Hakan Karatas 2013, using a bubbling fluidized bed gasifier showed that increasing the air feed of equivalence ratio (ER) reduced the syngas quality. The concentrations of CO and CO_2, both CH_4 and H_2 increase with decreasing ER. The H_2 composition in the syngas decreased from 20.01% to 5.05% when the ER was increased from 0.15 to 0.45. Similar thermal behaviour was observed in A. Ongen et al. 2019. This intern has a negative impact on the LHV of the product gas as well as the cold gas efficiency of the gasifier. However, in a study by Mavukwana 2016, lower ER values lowered the bed temperature which reduced the yield of gas. Thus, steam addition at higher ER was shown to improve the LHV and quality of the syngas. The optimum ER was shown to be 0.33. Serrano et al [189], using a bubbling fluidized reactor observed that the LHV reduces from 8.2 MJ/Nm3 to 5.3 MJ/Nm3 when ER is increased from ER = 0.16 to ER = 0.33. carbon conversion and LHV rose by 7.2% and 0.75 MJ/Nm3, respectively when temperature was elevated from 700 to 850 ◦C. This study's most notable finding was that the amount of short-chain hydrocarbons ranges from 5 to 13%vol on a nitrogen-free basis. Half of the LHV product gas was composed of short-chain hydrocarbons, which reached 11.97 MJ/Nm3. If the contribution of these chemicals is taken into account, the typical gasification findings published in the literature may be improved.

Numerical and experimental studies by [31,190,191], show that steam gasification represents the best choice for the utilisation of waste tires. Donatelli et al [191], using a rotary kiln showed that the energy content of the product gas is affected by the steam to waste tire feed ratio (FR). When increasing the steam feed ratio, the reforming reactions are favoured which improves the quality of the syngas. The optimum syngas with heating value (LHV) of 29.5MJ/kg$_{gas}$ and a composition of 52.7%vol H_2, 18.1%vol CO, 7.0%vol CO_2, and 22.2%vol CH_4 (N_2 free) was achieved at a moderate FR of 0.33. This means that at FR of 0.33 the reaction reached the stoichiometric limit for the considered process conditions. Experimental results revealed that increasing the FR required a greater amount of input energy to raise the temperature of the steam to the process temperature, but also tripled the CO_2 emissions. Detailed studies on parameters affecting the gasification of waste tires are found in [17,188,192]. These researchers concluded that the choice of the gasification agent depends on the desired quality of the syngas, ratio of H_2/CO, LHV of the gas, the concentration of tar, and the yield of char. Steam produces a higher concentration of H_2 and CH_4, which lead to higher LHV of the syngas. However, steam gasification is an endothermic process, and more heat is required to main the desired gasification temperature. It is therefore advised that the quantity of steam used should not exceed the stoichiometry requirements to reduce the energy required and maximize the LHV of the product gas. Wheres ER above 0.45 leads to a decrease in both yield and production rate of product gas while increasing the CO_2 production rate. Labaki [192], recommends the use of air and CO_2 as gasification agents to overcome the problems associated with low gasification temperature for steam and low LHV for air only. However, this also leads to a decrease in hydrogen production. The conclusion is thus, waste tire gasification parameters should be optimized according to the required properties of the syngas and type of equipment to be used [192].

Recent research in waste tire gasification focuses mainly on the production of heat and power, as well as the synthesis of liquid fuels, natural gas or pure hydrogen from tires. Syngas has a large range of applications in energy and chemical production. The following section 5.2.1 reviews studies dedicated to the improvement of syngas characteristics to have the desired composition for further application. Section 5.2.2 reviews applications of syngas.

2.5.8 Effect of catalyst and co-gasification with biomass and CO_2

Early studies by [28,113,193,194], revealed that catalytic gasification in the presence of catalysts such as Ni/Alumina and Ni/dolomite increases the yield of syngas gas, as well as the composition of hydrogen in the gas, is increased. When using the Ni/Al_2O_3 the gas yield was increased from 39.8 to 61.2 wt.% while the tar yield was reduced from 31.9 to 8.7 wt.% when the catalyst loading was quadrupled. Authors speculate that the presence of catalyst enhances the steam reforming reactions. However, the hydrogen yield was shown to decrease with an increase in the bed temperature. Again, the authors speculate that the reverse water gas shift reaction at gasification temperature less than 800°C dominates over the reaction of decomposition of hydrocarbons which resulted in lower concentrations of H_2 and a higher concentration of CO. These authors also showed that 5% Ni loaded on calcined dolomite catalyst increased the gas yield was significantly from 30.3 to 49.1 wt.% and the potential H_2 production was significantly increased when the Ni content was increased to 20%. However, in both studies, the presence of sulphur is reported to increase the formation of coke on the catalyst thus reducing the H_2 production potential of the process. Increasing the steam feed ratio as well as the catalyst: waste tire ratio seems to reduce the coke formation problem. In [18], the influence of steam and catalyst position (in-situ and ex-situ) on waste tyre gasification was investigated. Four different catalysts were test by adding the catalyst (olivine and dolomite) directly to the feed (in-situ), and another by using a secondary (ex-situ) catalytic stage (Ni/olivine and Ni/Al_2O_3/CaO). The gas yield increased from 60.8% w/w for the sole tire gasification to 63.5% w/w with olivine and 84% w/w with dolomite for the two in-situ catalysts. The production of hydrogen increased from 51.6 vol% for sole tire gasification to 65.6 vol% for dolomite and 57 vol% for olivine. According to the data, olivine has a greater effect on char formation, but dolomite has a greater effect on gas yield. The Ex-bed catalysts produced a high yield of hydrogen-rich gas under both dry and steam reforming conditions; a commercial nickel alumina/CaO catalyst was more effective than a Ni-olivine catalyst for syngas reforming. In particular, under circumstances of steam reforming, the highest hydrogen content of the nickel-alumina/CaO catalyst is 74 vol%. A recent study by Wang et al [195], investigated the influence of catalyst (Ni/Al_2O_3) position during the CO_2-assisted gasification of polypropylene. Their results revealed better catalytic activity for the quasi-in-situ configuration in the thermal decomposition of PP into H_2 and C_mH_n than in-situ catalytic configuration. Mario Toledo 2018 used a hybrid filtration reactor with alumina spheres to investigate the effect of gaseous agent flow on the yield of syngas. Pure air as a gasifying agent was shown to produce the highest concentrations of H_2 and CO. This was linked to thermal behaviour of the reactor; wherein high temperatures of the reaction wave led to increasing syngas yield. The addition of steam or natural gas had no positive impact on the syngas production performance of the hybrid reactor.

In a study [196], waste tires were catalytically gasified with subcritical and supercritical water to produce hydrogen-rich syngas in a tubular batch reactor. The high yield of syngas and H_2 was achieved at a temperature of 625 °C, 25 MPa, and 60 min residence time and 5wt% water in feed. Prolonged reaction times promoted the cracking reactions which increased the production of permanent gases. The Ni/SiO_2-Al_2O_3 catalyst resulted in the highest H_2 yield compared to the hydroxide catalyst. However, the hydroxide catalyst demonstrated a high potential to absorb the CO_2 evolved during hydrothermal gasification. These authors measured the performance of the process using parameters such as the carbon gasification efficiency (CGE), which is moles on carbon in the product per moles of carbon in the feed. The optimum CGE achieved was 35%, which simply means the system produce more liquid oil than the target gas. The low temperature may have contributed to this, higher temperatures than 625°C would have resulted in favourable yields towards the gas. Their finding suggests that waste tires can be converted to a hydrogen-rich syngas at lower temperatures than normally recommended. Hydrothermal gasification is also shown to have the potential to yield fine chemicals and solvents (e.g phenol, caprolactam acetone etc.). Studies by [197,198], suggest that high-quality liquid products and energy can be recovered from waste tire through subcritical and supercritical water thermolysis process. The use of hydrothermal gasification of waste tires with sub/supercritical water is an area of study that is still underdeveloped.

Despite this, catalytic gasification has not found complete industrial application due to increased costs and issues associated with catalyst synthesis and recovery. Coking occurs due to cross polymerization and cracking reactions during gasification, and this reduces the activity catalysts used. Therefore, this problem must be considered when designing systems that utilise catalyst. Using Industrial waste with catalytically active chemicals can solve these issues. Earlier in section 5.1, the spent fluid cracking catalyst which is a by product for the petroleum industry can be using during gasification of waste tires. While there have been published studies on the thermal cracking of tire pyrolysis oil and tire pyrolysis utilizing FCC, the utilization of FCC during gasification is still absent.

Policella et al [199] showed that quality of syngas can be achieved with CO_2 assisted gasification and such configuration has the potential to mitigate two environmental pollutants (CO_2 and waste tires). In this study, the authors compared pyrolysis and gasification based cold gas efficiency (CGE) and overall energy efficiency wherein the electrical energy input is considered. Unsurprisingly gasification provided the highest yield of CO gas up to 3.3 times that of pyrolysis whilst consuming almost 0.75g of CO_2 per gram of waste tires. However, the presence of CO_2 also decreased the yields of CH_4 and C_2 hydrocarbons which reduced the LHV of the syngas. This meant that from an overall energy efficiency point of view, (At 1173 K) pyrolysis performed better at 38% compared to 30% for gasification. CO_2 contributes to better syngas quality but showed slow reactivity on even at a higher temperature. Czerski et al [141] used different biomass ashes as catalysts to promote tire char reactivity during CO_2 gasification. The results showed that biomass ashes enhanced reactivity of tire char by shifting the conversion curves of the CO_2 gasification process towards lower temperatures and significantly improve the reactivity indicators, such as the reaction order n. While biomass ashes had a positive effect on CO_2-tire char, coal fly ash affected the tire char reactivity. The present of K_2O, MgO and P_2O_5 in the biomass ashes was touted as responsible for tire char reactivity. Lahijani et al [200] results also suggest that CO_2 assisted gasification is effective on char reactivity when tires are blended with biomass. These authors concluded that the presence of the inherent alkali and/or alkaline earth metals in biomass fuels act as natural catalysts to enhance the gasification rate of tire char. Results signified the incidence of synergy during CO_2 gasification of TC/biomass blends. [142], showed that the effectiveness of CO_2 on pyrolysis of waste tires is enhanced when using steel slag as a catalyst. This impeded the formation of pyrogenic compounds thus enhancing the production of H_2 as well as CO. Jansen et al [201] investigated the influence boudouard reaction during waste-tyre pyrolysis and gasification of scrap tyre rubber crumbs under nitrogen and treatment with pure carbon dioxide. The conclusion drawn from this study is that CO_2-C = CO is active between from 750 ◦C to 1100 ◦C. And reaction is diffusion controlled in that the rate of chemical reaction at the particle surface controls the Boudouard reaction, and this rate is directly proportional to the particle radius. Another study [202] showed the C-CO_2 reaction is slow due to the mass transfer limitation caused by the intraparticle diffusion of CO_2. Pore size influences the diffusion rate of CO_2. At higher temperatures, the pore size of the char increases allowing more CO_2 to diffuse thus improving CO_2 gasification. Sadhwani [202] showed that in CO_2-asssited gasification of biomass, increase in temperature from 850 °C to 934 °C increased both the surface area of char micropores from (237.7 m^2 /g) and total pore volume (0.06202 cc/g) to surface area (350.5 m^2 / g) and pore volume (0.1428 cc/g).

In a study by [6,160], pine bark were co-gasified with waste tires using CO_2 at 800 °C and 900 °C. The results showed increasing both the biomass blend and CO_2 improved the syngas yield and quality of syngas. Between 0.85 to 1.1 ton of CO_2 is consumed per ton of waste tire-biomass mixture. This result provides a viable carbon offsetting pathway whilst mitigating two solid waste streams. From an energy point of view, increasing in pine bark blend decreased the energy output at both temperatures. The energy of syngas is linked to the presents of C_mH_n, at higher temperatures and pine bark blends the yield of C_mH_n decreases, this intern reduces the syngas LHV. The authors found that higher temperature gasification requires an increase in energy input with an insufficient advantage in terms of syngas yield and this decreases the energy recovery efficiency. These results are in agreement with the findings of [203], who showed that co-gasification of solid materials (wood, weed, tires, and carton) suppresses the formation of tar and char formation but improved the yield, quality and properties of gases. Recent studies have shown that when different feedstocks are co-gasified in CO_2-astmosphere improved product quality, energy efficiency, and poly-generation of products for market flexibility are realized [200,204–215]. The presented literature is of significant practical importance regarding the possibility of using waste materials such as biomass as catalysts for the gasification of low-reactive tires. Lacking are studies investigating the synergy of co-gasification of plastic polymers and wate tires. While research on the nonlinear interaction between polymer wastes and biomass/coal have been published with a few different types of plastic, none have yet been conducted with waste tires [20]. However, all referenced studies suggest that co-gasification increases the quality of syngas while decreasing the amount of CO_2 emissions. The authors show have also shown that CO2 gasification increase the yield of syngas and this is because of tire Char-CO_2 reduction reaction [216,217]. The results reported herein therefore clearly demonstrate the synergistic interaction between waste materials to recover valuable products and reduce the carbon footprint.

2.5.9 Simulation and techno-economic analysis of chemicals and power production from tires (IGCC)

The demand for environmentally friendly fuels is increasing around the world and it was mentioned earlier in section that syngas provides the perfect intermediate raw material to produce multiple products such as diesel, gasoline, methane and hydrogen, methanol, dimethyl ether (DME), ethanol, olefins, waxes, ammonia, electricity and more importantly hydrogen. This section combines the simulation studies as well as economic analysis of waste tyre gasification technologies. Simulation provides the means to assess the potential of process in the early stages of design or conceptual stage before expensive investments on experimental tests and construction is conducted. During this stage techno-economic analysis are also conducted.

In [218] Aspen Plus V10 simulation environment was used to evaluated the co-production of syngas and activated carbon in three reactor configurations: fluidized bed, fixed bed, and rotary kiln at the systems level. A combination of semi-empirical model and Gibbs free energy minimization model was used to build the fluidized bed reactor while the fixed bed and rotary kiln were based on a combination of kinetic model and Gibbs free energy model. The effect of parameters equivalence ratio (ER), steam to tire ratio SFR) on LHV, syngas, carbon conversion, cold gas efficiency and activated carbon yields was investigated. For the three reactor configurations, ER = 0.3 and SFR = 0.25 were found to be the optimal feed conditions for co-production of syngas and activated carbon. At these conditions, (1) the fluidized bed gasifier can produce syngas with a low heating value (LHV) of 6.67 MJ/Nm^3, cold gas efficiency of 82.4%$_{LHV}$, AC with BET surface area of 698.63 m^2/g, and a carbon conversion ratio of 92.5 %, (2) the fixed bed gasifier has a syngas LHV of 6.25 MJ/Nm^3, CGE of 85.9%$_{LHV}$, AC with BET surface area of 432.51 m^2/g, and CCR of 96.8%, and the rotary kiln gasifier has 5.96 MJ/Nm^3. Although the model was sufficient to describe the processes, we dispute that the carbon conversion should exclude CO_2 as the product in the syngas in order to determine the actual carbon emission of each individual process (CO_2/kg or tire feed).

Ma et al [219] use thermodynamic analysis to investigative conversion of waste tires to syngas using a plasm gasifier. A model was built on Aspen Plus ® simulation software system and the effect of air, steam on hydrogen production was investigated. The effect of carbon capture on the system efficiency was also investigated. The plasma gasification using steam and air as gasification agents achieved a carbon conversion rate, energy recovery rate, and exergy efficiency of 99.12%, 93.67%, and 80.04%, respectively. Adding the carbon capture reduced the exergy of system, and authors recommended that the best system for hydrogen production was the one utilizing steam and air as the gasification agent and integrating the Rectisol process for achieve carbon capture. This process had a total exergy efficiency of 36.45%. Kartal and Ozveren [220] use Aspen Hysys to build a waste tyre fuelled integrated gasification combined cycle (IGCC) with an entrained bed gasifier/GT/Kalina cycle that uses CO_2/air for the gasification process of the biochar/waste tyre blend. The authors investigated the effect of CO_2, turbine pressure, gasification temperature and air ratio (ER) on energy and exergy of the system. The authors concluded that the optimal air ratio was $0.23 > ER < 0.25$ achieved the highest overall system energy efficiency > 85% and overall exergy efficiency of 80%. CO_2 concentration in gasification agent about 5%< CO_2/air ratio < 7.5% achieved the highest energy and exergy efficiency. The ideal value for the Kalina turbine inlet pressure was set at 28 bar. Gasification temperature above 1300ºC had significant impact on the overall energy efficiency. Authors did not conduct an economic analysis of this system.

In Subramanian et al [23], a combination of experimental data and commercial process simulation software (ASPEN Plus) were utilised to evaluate the thermodynamic, economic and environmental performance of a rotary kiln gasification process to produce liquified synthetic natural gas (methane) from waste tires. Three design cases (without CO_2 Capture and Sequestration (CCS), with precombustion CCS and with pre- and post-combustion CCS) were investigated. The production of methane from syngas proceeds via hydrogenation of CO and CO_2 over a metal-based catalyst according to the methanation and Sabatier reactions and the stoichiometric requirement for syngas gas hydrogen to CO ratio is required to be above three.

The authors in this study chose the rotary kiln reactor as it can achieve a waste tire-derived syngas with a high H_2: CO ratio of 3.77. This eliminates the need for an inefficient reverse water gas shift step. The thermodynamic analysis result shows that for each kg of waste tire converted, 0.37 kg of liquefied methane is obtained, this translates to a cold gas efficiency of 54.2%. However, when using the overall energy efficiency (including utilities and electricity), the performance of the process reduces to a maximum of 43.6% (without CCS). The total CO_2 emissions dropped from 1.76 million tons per annum to 0.05 million tons when both pre and post-combustion CCS was utilised, however, there is a penalty for including the carbon dioxide capture and sequestration. The overall energy efficiency dropped to 39% due to the high electricity and steam requirements for the CCS systems. Economic analysis results showed that minimum selling prices of the syngas were between 16.7-24.9 $\$/GJ_{LHV}$ far higher than the standard selling prices conventional natural gas which range from 2.90 $\$/GJ_{LHV}$ to 9.85$\$/GJ_{LHV}$.

In Zang et al [32], thermodynamic and kinetic models were employed to investigate two commonly used gasifier technologies namely the fluidized bed and fixed bed to determine the most economical and efficient pathway for producing syngas from waste tires. Thermodynamically the fluidized bed gasifier was shown to perform better than the fixed bed, however, the fixed bed technology had the lowest Levelized cost of syngas, indicating that it would be the most economic pathway for syngas production. However, both technologies produced syngas with an LHV of 2.5-7.4 MJ/Nm^3, much less compared to the natural gas LHV at 35.8 MJ/Nm^3. Furthermore, the Levelized cost of syngas produced from waste tire gasification was found to be comfortable lower than the market price of natural gas, which indicates that waste tires are a potential source for syngas production. In contrast, a study by [186], showed that gasification of the waste tire in a fluidised reactor produced gas with a heating value ranged between 39.6 MJ/Nm^3 and 22.2 MJ/Nm^3, corresponding to a gas yield ranged from 0.21 Nm^3 /kg to 0.76 Nm^3/kg.

Ozonoh et al [221,222], postulate that the co-gasification process using a fluidized bed system can archive an overall energy efficiency of about 40%-50% and reduce the cost of feedstocks used for electric and thermal power generation. Consequently, a techno-economic analysis of electricity and heat production, as well as environmental impact assessment of co-gasification of coal, biomass and waste tire in 5MW co-gasification power plant was evaluated. The economy of the plant was evaluated with feedstock costing (WFC) and without feedstock costing (WOFC), as well as the NPV, IRR and PBP were utilised for the profitability analysis.

The results showed that a 50% reduction in CO_2 emissions is achieved when a coal-to-solid waste ratio of 1:1 is employed instead of Malta coal. Increasing the coal ratio increased emissions. However, the economic analysis was not conclusive, the authors report that using the Malta Coal + Pine sawdust at blend ratio 1:1 is the most attractive for WFC while the use of Malta Coal + Waste tires at a blend ratio of 1:1 is the most viable option for WOFC. Currently, in South Africa the waste tire management is in disarray, meaning the availability of tires as feedstock at almost zero cost and the government will provide transportation and storage.

Hasan and Dincer [33], used the Integrated Gasification Combined Cycle (IGCC) to assess waste tires as a feedstock for hydrogen and power production relative to other solid fuels (i.e. coal and biomass). The effect of operating conditions on system performance, hydrogen production and carbon dioxide emissions were assessed for each type of feedstocks. The authors concluded that the energy and exergy efficiency of the overall system was 55.01% and 52.31% when tires were used as feedstock. The maximum hydrogen production to tire feed rate ratio achieved was 0.158, which was comparative to that of coal at 0.161. The carbon dioxide emissions were slightly higher for tires (32.16kg/s) when compared to coal (31.06kg/s), but lower when compared to biomass (33.35kg/s). However, their result shows that waste tires can be used as a potential feedstock for hydrogen production, which can contribute to reducing the environmental impact and provide better sustainability.

Machin et al [223], investigated the technical viability to produce electricity and thermal power from tire derived fuel (TDF) gasification using two technologies namely an internal combustion engine driving a generator (ICE-G) and a gas turbine driving a generator (GT-G). Their results show that the internal combustion engine-generator combination is more efficient (21.4%) to generate electricity when compared to gas turbine-generator configuration (16.91%). The internal combustion engine produced 1.49 MW electricity compared to 1.18 MW produced by the gas turbine. However, when the thermal energy carried by the exhaust gas was considered, the gas turbine outperformed the internal combustion engine. the thermal efficiency of the GT-G was higher (60.58%) than that of the ICE-G, at 53.85%. The total power generation in the GT-G is thus slightly higher (77.49%) than the total power generated in the ICE-G (75.25%). In both cases, the heat recovery steam generator was not considered. However in a similar study [224], the authors considered the IGCC (Integrated Gasification Combined Cycle), and they showed that the IGCC produced up to 16.1 of electric energy per kg of waste tires compared to 8.2 MJ per kg produced by the ICE-G. The latter results are in line with the analysis done by [81] The internal combustion engines (ICE) underperforms when compared to the combined cycle (IGCC).

Oboirien and North [17], provided a comprehensive review of all experimental and pilot-scale waste tire gasification studies dating from the year 2000. The study revealed major gaps in knowledge and some of the findings were:

- There is minimal information on solar-assisted gasification of tires.
- There is still a need for a comparative study on plasma gasification, especially co-gasification of tires and other solid fuels such as biomass and studies on the use of a catalyst in plasma gasification.
- A comprehensive comparative techno-economic analysis of waste tire gasification is required to assess the different possible product that can be produced from waste tires.
- There is still insufficient information on the optimal conditions to produce syngas, hydrogen, and carbon nanotubes and other value-added carbon products from tires.

When it comes to assessing the viability of waste tyre thermochemical conversion processes, Subramanian et al. [225] and co-workers [226,227] have been the most innovative. These authors constructed a polygeneration superstructure process to capitalize on synergies between waste tires and other feedstocks and to provide the flexibility to switch between target products and alternate production rates in response to market demands and price fluctuations. The method relies on waste tire gasification to produce syngas. The syngas derived from tires is split into three branches that lead to the power generation, methanol synthesis, and methanation systems. Methanol products are used to produce DME and olefins as an alternative to selling it in its pure form. The authors conducted a techno-economic analysis of the superstructure process in such a way as to highlight the impact of varying product prices and CO_2 taxes on the optimal design and operation of the process. The research involved three distinct sets of independent simulation steps. For each process section's mass and energy balance calculations, Aspen Plus and Aspen Hysys were utilized. Next, the ALAMO software package was utilized to fit surrogate models that consist of algebraic equations relating input and output variables for each process section. Lastly, Mixed-Integer Nonlinear Programming was used to calculate the net present value (NPV) for each process section by linking the GOSSIP and ANTIGONE solvers. In one scenario, waste tire tipping fees of $100/tonne were considered as revenue, whereas in the other scenario, they were disregarded. The findings indicate that the imposition of tipping fees increases the utilization of waste tires, which in turn suggests that designs that favor the production of methanol or DME are optimal for a wider range of product prices. However, the initial capital investment excess of 800 million dollars will not attract investment for a waste material, also the methodology did not indicate the payback period as well as internal rate of return.

Although the aforementioned studies highlight the value of using a hybrid of conventional and alternative feedstocks in general, a simplified approach is required that that can give a definite answer to policy makers and investor as to which process is best for waste tires in all conditions. Additional research is required to analyze the co-utilization of waste tires with other feedstocks such as biomass, plastics, and the use of tires in the production of iron and steel.

2.6 Gaps in knowledge

There is substantial literature on gasification and pyrolysis of waste tyres and this literature study could not cover all but selected the best first of its kind studies area of interest. The literature studies indicate the potential of pyrolysis and gasification to convert waste tires into valuable chemicals and power, however despite such extensive studies on tires there is yet to be an established technology to tackle the increasing number of tires. In the developed world, waste tire rate generation is estimated to be equivalent to one waste tire per person each year and no built technology can meet this rate of generation. There is the need for a novel approach to screen waste tire processes based on the conservation of the material, energy efficiency and emissions. Based on the above literature the major research on waste tires focuses on investigating the optimum operating conditions to produce syngas, tire derived liquid oil, char from tires. Key parameters mostly studied are temperature, catalyst, co-pyrolysis and co-gasification with other waste or biomass, oxidising agent and feeding ratio. Major topics currently addressed are:

(1) Maximising the limonene concentration in the tire derived oils [19,85,92,96,133].
(2) Maximising hydrogen production via catalytic pyrolysis [114,135,143], gasification [28,194,196] and integrated gasification cycle combine [33].
(3) Pyrolysis characteristics and mechanism [7,91,145,228,229].

(4) Tar reduction to maximise syngas [18,28,208].
(5) Manufacture of activated carbon and carbon nanotubes [114,134].
(6) Co-pyrolysis and gasification with biomass and CO_2 to the maximum liquid oil [161,164,165,230] and hydrogen production [6,199].

Many of these studies do not show the direction towards the development of a process to tackle the arising waste tire problem. Tires are still limited by poor char reactivity and huge product spectrum that require extensive downstream processing. The gas product contains over 25 hydrocarbons, the liquid oil contains over 100 hydrocarbons comprising of PAH, olefins, paraffins, etc all in less than 4 wt% composition each. The char has very poor surface area and pore sized to be considered activate carbon. Although significant studies on downstream processing are available, the cost associated with this is still unbearable to the investment. Therefore, research on how to improve the pyrolysis products and gasification products within the reactor is still ongoing.

The challenges identified are that the generation of CO_2, soot and tars are still a major barrier to the commercialisation of waste tire thermal processes and inadequate work has been done on the techno-economic analysis of waste tire processes with only nine on pyrolysis and only 7 relevant studies on gasification thus far. Significant work has been done on chemicals and power production from tires. Available studies are on methane, methanol, syngas, hydrogen, olefins and electricity [17,33,221,222]. There should be studies on ammonia, petroleum fuel, and other chemicals must be put under the same analysis to have a full picture.

The following area of research areas still need to be covered.

1. Co-gasification of tires with more feedstock that can unlock the reactivity of tire char.
    a. Co-gasification of tires with spent FCC is still lacking.
    b. Co-gasification and pyrolysis of waste tire with plastic waste is still lacking.
    c. Catalytic co-gasification of waste tire and plastics for a polygeneration system to meet the demand.
    d. Co-gasification of waste tire with alternative oxygen carries such as waste gypsum ($CaSO_4$).

2. More studies on the production of liquid chemicals via gasification-More research is required to determine valuable process routes to convert tires to value-added products. Much of the research focus merely on syngas an intermediate raw material, however by evaluating the overall liquid fuels process the cost of producing syngas can be covered by the revenue generated from the sale of the fuels. Processes such as:
    a. Co-production of methanol and iron ore reduction from waste tires
    b. Thermodynamic, economic, and environmental performance of co-production of ammonia and electricity.
    c. Polygeneration scheme of hydrogen or petroleum fuels with power and fertilizers.
    d. Co-production of dimethyl ether (DME), and petroleum liquid fuels and electricity via co-gasification of tires.
    e. Solar assisted pyrolysis and gasification- with only a total of six reports on solar assisted thermochemical conversion of tires, more research in the area is required to fill the gap on the optimum conditions for solar assisted conversion of waste tires.
3. Therefore, a comprehensive comparative techno-economic analysis of the processes mentioned in 2 is required to assess the most commercially viable route for tires.
4. The supercritical/subcritical gasification of waste tires is still an under studied-there is a need to establish a database of hydrothermal gasification of tires to establish the optimum conditions.
5. Waste tire pyrolysis- This area of research is well established, however, there is a need to determine the optimum conditions for secondary upgrading of pyrolysis products. Synergy of co-pyrolysis with other feedstock to improve products yield is required.
6. More research that looks at the transformation of tires from a system point of view, thus integrating all equipment involved is required. Overall system analysis uses

thermodynamics to determine the limits of performance in terms of the material going in and out of the process as well as the energy, both in quantity and quality, involved in the transformation. The goal is to optimise the system as a whole rather than focusing on the small details of individual units.

2.7 Concluding notes

Thermal treatment procedures such as pyrolysis and gasification to liquid fuels have been thoroughly researched, and it has been discovered that it is feasible to reduce tire pollution. It is feasible to save existing resources and recover usable goods such as gasoline, char, chemicals, and steel by using discarded tires. The following conclusions are drawn from the extensive literature reviewed:

1. Co-gasification and pyrolysis of waste tires with alternative waste materials such as FCC, gypsum, plastics polymers have not found traction.
2. A techno-economic analysis is required to compare the use of gasification/co-gasification of waste tires with other solid-to-liquid processes. This will indicate the highest value process pathways for chemical conversion of tires.
3. A system analysis approach is required to determine the limits of performance of these processes in terms of the material going in and out of the process as well as the energy, both in quantity and quality, involved in the transformation.

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3 Comparison of pyrolysis and gasification of waste tires: Process synthesis approach

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Short Summary

The global tire demand is expected to grow by about 4.9% per year to 3.2 billion in 2022, with this demand also scrap tire waste increases. Therefore, there is a need to increase recovery means. So far, we have established that globally thermochemical conversion processes have a potential to consume the total available waste tire resource and convert it to high value chemicals and fuels. However, even with these, there is no single set of optimal conditions that can achieve a predetermined product quality within the set environmental limits. There is the need for a novel approach to screen waste tire processes based on the conservation of the material, energy efficiency and emissions. In this paper process targeting and process synthesis techniques are used to identify performance limits for the conversion of waste tires to valuable products. Two thermochemical conversion processes of pyrolysis and gasification are evaluated on the production of synthetic fuels and solid carbon, the two thermal treatment processes of are evaluated in terms of the fundamental thermodynamic metrics of carbon efficiency, atom economy, e-factor and chemical potential efficiency, and also their market-related revenue potential. It was found that pyrolysis pathways perform better in terms of thermodynamic efficiency and carbon footprint than gasification processes, which lose about 45% of the carbon feed to carbon dioxide. However, the gasification routes offer higher potential revenue, yielding as much as $625 per ton of waste tire as compared to $205 from the pyrolysis route. Based on these results other alternative gasification routes that produce other chemicals and power are further analyzed in detail in the subsequent chapters of this dissertation. The process synthesis method used in chapter 3 forms the basis of all analysis from hence since it establishes the potential of a process pathway in a universal way that is independent of the specifics of process design and optimization, thus making it possible to do long-range planning based on fundamental thermodynamics rather than the limitations of current process design. This approach is better suited to long-range planning, not only for research engineers but also for legislators and long-term investors, because it gives an indication of future prospects.

Declaration by canditate:

The scope of my contribution to the chapter are as follows:

Planning of simulations	60%
Conducting the simulations	80%
Results interpretation	70%
Compilation of the chapter	100%

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I declare that the above information is true and reflects the nature and extent of the contributions of the candidate and the co-authors

Signature of candidate:………………………… Date:…14/03/2023…

Thermodynamic comparison of pyrolysis and gasification of waste tires

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Abstract

Waste tires are a particularly problematic pollutant; persistent, highly toxic, flammable, and difficult to process or store. However, waste tires need not be viewed solely as a waste material, as they also offer promising properties as an energy material. Waste tires have a higher energy density than coal, as well as lower ash content and favorable quantities of carbon and hydrogen. Extensive experimental research has demonstrated that thermochemical valorization pathways including pyrolysis and gasification are viable for producing valuable chemical products from waste tires. Despite this, there is as yet no established technology for waste tire conversion. In this paper, fundamental thermodynamic and economic analysis is used to evaluate a range of process pathways to determine their economic favourability and environmental impact. The process performance targets derived in this way can serve as a basis for preliminary process design and provide estimates for the commodity value of waste tires, informing long-range planning in both corporate and legislative settings. A range of pyrolysis and gasification pathways have been evaluated in terms of the fundamental thermodynamic metrics of carbon efficiency, atom economy, e-factor, and chemical potential efficiency, and also their market-related revenue potential. It was found that pyrolysis pathways perform better in terms of thermodynamic efficiency and carbon footprint than gasification processes, which lose about 45% of the carbon feed to carbon dioxide. However, the gasification routes offer higher potential revenue, yielding as much as $666 per ton of waste tire as compared to $202 from the pyrolysis route.

Keywords: Waste tires, pyrolysis, gasification, thermodynamic and economic analysis

3.1 Introduction

It is estimated that there are over 60 million waste tires stored in depots across South Africa with a further 11 million added each year. The total potential supply of waste tires is thus estimated at 177 124 tons annually [1]. However, factors such as environmental concerns, high energy cost, low market value and product demand are limiting the development of commercially viable waste tire recycling technologies. Thus, it becomes more economical to simply landfill end-of-life tires rather than recycle. However, landfilling waste tires comes with some major environmental issues including contamination or blockage of waterways, accidental fires, and breeding sites for mosquitos and rodents.

Thermal valorization through pyrolysis and gasification are the most promising pathways to transform waste tires into useful energy and other chemical products [2,3]. There are numerous sources of existing research that focus on the optimization of these technologies. Recent research [2,4–9] have revealed the potential of pyrolysis as a waste management process for tires.

Pyrolysis of tires produces three primary products, namely char, liquid oil and non-condensable gases that can be used as fuel or chemicals in many industrial applications. The studies effectively evaluated the considerable effects of the reactor temperature, heating rate, catalyst, and reactor configurations on the products and conversion rate. However, the studies also revealed that there are no universally recommendable pyrolysis conditions to yield the desired output, which varies with reactor configurations, and type of tire used. This makes it difficult for industrial application.

The other observed drawback is the quality of the product produced; the liquid oil (TPO) is a mixture of many valuable chemicals such as dipentene (limonene), benzene, toluene, xylenes, ethylbenzene, and other monomers of the rubber that can be recycled. However, these components are present in small concentrations and have similar physical properties (boiling point) such that it becomes costly to separate them. This makes the TPO unattractive for further use except as a low-quality additive in heating oil or bunker crude.

Char is a heterogeneous material with regards to the ash content, particle size, absorption properties, structure and both surface chemistry and activity, and cannot be sold directly as activated carbon or carbon black which affects the economic feasibility of tires. However, internationally the pyrolysis process is one of the most used technologies to recycle tires, and all current research is focused on the beneficiation of char and the upgrading of pyrolysis oil to improve the industrial viability of waste tire pyrolysis.

Another comprehensive review by [10] revealed that gasification is another route that can be utilised to achieve 100 % conversion of waste tires. Gasification is a mature thermochemical conversion technology in use since the 1800s that uses sub-stoichiometric air (or oxygen), steam, heat, and pressure to convert organic substances to syngas, a mixture of carbon monoxide and hydrogen. Syngas is an essential intermediate material for the conversion of a number of carbonaceous raw material to electricity, liquid fuels and the synthesis of ammonia, methanol and other related products.

However, as discussed in that paper, there are significant knowledge gaps that limits the adoption of this technology. A detailed study that compares the yield of syngas, hydrogen, and carbon products from tire gasification is required. A comprehensive comparative techno-economic analysis of waste tire gasification is required to assess the different possible products that can be produced from waste tires. There is a need to optimise the conditions for the production of hydrogen, syngas, carbon nanotubes and other value-added products [10]. The goal of the research being presented in this work is to lay the foundations for filling this knowledge gap. We follow on the findings of [10] and perform a comparative study of waste tire gasification and pyrolysis pathways to assess the different possible products that can be produced from waste tires. Process targeting and process synthesis techniques will be used to identify performance limits for the conversion of waste tires to valuable products [11–13]. This approach seeks to set all the gasification and pyrolysis processes at the same basis and assess their performance by looking at their specific material balances their theoretical energy and work requirements. This can reveal feasible solutions and opportunities for using waste tire more effectively as a source for energy and chemicals. Suitable ways of providing energy to the processes will be investigated. These results will provide an overview of the technical and economic benefits of the different process pathways and serve as a basis for decision making in the development of waste tire conversion processes.

Although much of the studies on the chemical transformation of waste tires are focused on improving single unit operation through the investigation of key operating parameters such as temperature, catalyst, etc. Minimal research has looked at the transformation of tires from an overall system point of view, thus integrating all unit operations and equipment involved. Overall system analysis uses thermodynamics to determine the limits of performance in terms of the material going in and out of the process as well as the energy, both in quantity and quality, involved in the transformation [14]. The goal is to optimise the system as a whole by first identifying feasible targets and selecting optimum targets based on specific criteria in terms of material, energy and work efficiencies rather than focusing on the small details of individual units. This approach is crucial for the early stages of the conceptual design of the process before the flowsheet exists, as it gives one global insight into what is achievable.

3.1.1 Systems analysis approach

For a process to operate at 100% raw material conversion efficiency and minimal impact on the environment, the law of conservation of mass implies that the elemental composition of the desired products must match that of the feed. Equation 1 shows that tires contain a ratio of carbon to hydrogen close one to one, therefore the eventual set of desired products (in combination), regardless of the process, must contain the same ratio of carbon to hydrogen, because any deviation would lead to the formation of unwanted products (i.e., CO_2), thus reducing efficiency. For example, in equation 1a, we show the conversion of a tire polymer to syngas using oxygen, where all carbon in the tire feed is transferred to CO and hydrogen. The tire polymer network is represented by empirical formula ($CH_{0.95}O_{0.02}N_{0.005}S_{0.007}$).

$$(CH_{0.95}O_{0.02}N_{0.005}S_{0.007}) + 0.502O_2 = CO + 0.475H_2 + 0.005NO_2 + 0.007SO_2$$

$$\Delta H = -52.672\,kW,\ \Delta G = -91.334\,kW \qquad [1a]$$

For the production of chemicals and liquid fuels from syngas a 2 to 1 ratio of H_2 to CO is preferred, and while other ratios are suitable for other process pathways, for the purposes of this preliminary study, it is sensible to use the 2 to 1 ratio as a target because it is the most universally applicable product ratio, being suitable for a range of different processes.

One can immediately see from the above equation that the gasification process, with the constraint of a complete conversion of tire to CO and H_2 and utilizing just oxygen, can never achieve the 2:1 ratio of hydrogen to carbon monoxide required for liquid fuel production. To achieve this ratio an additional amount of feed containing hydrogen often water is required, however often this additional feed comes in with an extra oxygen which must leave the system often as carbon dioxide. Also notable in equation 1a is that excess energy is produced, if this energy is not recovered either as thermal of electricity, this energy, along with its potential, will be lost. This will result in the process described in equation 1a unable to achieve the energy efficiency leading to a greater impact to the environmental.

When water only is used as an oxidant in order to increase the overall hydrogen content of the feed as shown in equation 1b, the process needs heat and work since water gasification is endothermic. This means part of the feed or product must be burned to supply the energy required. However, this leads to the formation of unwanted carbon dioxide.

$$CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 0.98H_2O = CO + 1.44H_2 + 0{,}007H_2S + 0{,}005NH_3$$

$$\Delta H = 228.984\,kW,\ \Delta G = 142.635\,kW \qquad [1b]$$

Since the gasification with oxygen produces excess energy and the gasification with water only requires energy, the most sensible approach implemented is to combine the two. Further material, energy and work integration is required to achieve the overall target of two to one hydrogen to carbon monoxide.

Therefore, chemical processes cannot be optimized through single units alone with the expectation of achieving an optimal process system. One must take into account the connection and interactions between unit operations of the system to achieve the global optimum. How can the material balance be manipulated to achieve the outcome, depending on the carbon and hydrogen in the feed and energy required by the process? The overall systems approach to process synthesis allows these questions to be answered in a broad way that is not dependent on a specific flowsheet.

In this work, the thermal treatment processes of gasification and pyrolysis will be investigated from the carbon efficiency, energy utilisation, and economic viewpoints. These measures of process performance are universal, and not subject to current market conditions, as financial and economic assessments are. The utilisation of raw materials, waste generation and the thermodynamic efficiency of the process will be assessed using the following four metrics;

$$Carbon\ Efficiency = \frac{moles\ of\ C\ in\ the\ desired\ product}{moles\ of\ C\ in\ the\ feed} \qquad (2)$$

$$Atom\ Economy = \frac{mass\ of\ desired\ product}{Total\ mass\ of\ feed} \qquad (3)$$

$$E - factor = \frac{Mass\ of\ waste\ produced}{Mass\ of\ desired\ product} \qquad (4)$$

$$Chemical\ potential\ efficiency\ (max) = \frac{\Delta G_{comb(desired\ product)}}{\Delta G_{comb\ (feed)}} \qquad (5)$$

Where G_{comb} is the Gibbs free energy of combustion reaction of a substance [15].

Equation 2 quantifies how much of the carbon in the feed stream ends up in the desired products. Any carbon that is not contained within a product will be lost in undesired by-products. Equation 3 and 4 also provide useful information on the utilisation of all the feed and waste generation. Equation 5 is the maximum chemical potential efficiency, which is a measure of how much of the chemical potential of the material is conserved during the chemical transformation to other products.

3.2 Methodology

The method used in this work requires two thermodynamic properties, i.e., the enthalpy (ΔH) and the Gibbs free energy (ΔG) data for waste tire, along with its molecular formula. However, a tire is a mixture of various components (polymers, plasticisers, metals, and other inorganic substances) in varying quantities, which means that tires do not have consistent thermodynamic properties.

For the sake of simplicity during preliminary this thermodynamic analysis, throughout paper, the waste tire will be treated as a single chemical compound rather than a mixture. The empirical formula of a single molecule of a passenger tire was calculated using the ultimate analysis presented in Table 3.1 [5] using a method was taken from [16,17].

Table 3.1. Ultimate analysis of waste tires [5]

Ultimate Analysis wt.%		***Proximate Analysis wt.%***		
C	*85.05*	*Moisture*	*1.14*	
H	*6.79*	*FC*	*32.28*	
N	*0.5*	*VM*	*62.24*	
O	*1.75*	*ASH*	*4.35*	
S	*1.53*	*LHV*	*34.9*	*MJ/kg*

The empirical formula for waste tires can be derived from the ultimate analysis in Table 3.1 of a passenger tire with the metals and reinforcement fabric removed, is represented as:

$$CH_{0.95}O_{0.02}N_{0.005}S_{0.007} \qquad (6)$$

This molecule is still complex and lacking in property data. The heat of formation was calculated to be $\Delta H^o = -59.77\ kJ/mol$ from the LHV of the waste tires as shown in equation 7 and 8.

$$(CH_{0.95}O_{0.02}N_{0.005}S_{0.007}) + 1.239O_2 = CO_2 + 0.475H_2O + 0.005NO_2 + 0.007SO_2 \qquad (7)$$

$$\Delta H_{reaction} = \Delta H_{products} - \Delta H_{reactants} = LHV(\frac{kJ}{mol}) \qquad (8)$$

The Gibbs free energy was estimated from the exergy of tires.

$$\varepsilon^o = \Delta G_f^o + \sum n_j \varepsilon_j^o \qquad (9)$$

The chemical exergy of tires was estimated using the lower heating value [16,17]:

$$\varepsilon^o = \beta LHV \qquad (10)$$

And $\beta = \frac{1.0412+0.2160\frac{z_{O_2}}{z_C}-0.2499\frac{z_{O_2}}{z_C}\left[1+0.7884\frac{z_{H_2}}{z_C}\right]+0.0450\frac{z_{N_2}}{z_C}}{1-0.3035\frac{z_{O_2}}{z_C}}$ (11)

Where, Z_{X_1} are the ultimate analysis values of tires, ε^o is the standard chemical exergy of waste tires, which is equal to the maximum amount of work obtainable from waste tires at standard conditions (298 K and 1atm). LHV is the lower heating value of waste tire, which is the net enthalpy of combustion of the tires.

The Gibbs free energy of the tires at standard temperature and pressure is found to be $\Delta G^o = -47.78\ kJ/mol.$

3.3 Results and Discussion

3.3.1 Pyrolysis to liquid fuels

Pyrolysis is a thermal degradation process of volatile matter in the absence of oxygen to produce three products; char, pyrolysis oil and a producer gas, which is a mixture of hydrocarbons and non-condensable gases. The yield of each fraction depends on process conditions such as temperature and heating rate. A brief literature review will show that when targeting the liquid oil, the operating temperature for waste tires is set between 425-500°C, producing a liquid fraction between 50-60 wt.% [18]. [19] showed that 475 °C is an appropriate temperature for the pyrolysis of waste tires, given that it ensures total devolatilization of tire rubber and a high yield of tire pyrolysis oil (TPO), of 58.2 wt.%, and char yield of 35.9 wt.%. The gas product was 5.9 wt.%, and it was predominately a mixture of C1 to C5 alkanes and alkenes, with varying contents of H_2, CO, CO_2 and sulphurous gases.

For this analysis, the liquid fuel and char are characterised by ultimate analysis. The thermodynamic properties of char and TPO are estimated with the same method used for tires. In the study by [18] the pyrolytic gas contains high yields of C1-C5 hydrocarbon, and the C_4H_6 (1-3, butadiene) fraction is present in high concentrations, it will represent all hydrocarbon gases formed for ease of calculations.

Using various literature sources [4,5,18,19], the following overall material balance for waste tire pyrolysis is approximated:

$$CH_{0.95}O_{0.02}N_{0.005}S_{0.007}{}_{tyre} = 0.551CH_{1.35}O_{0.035}N_{0.006}S_{0.006}{}_{oil} + 0.394CH_{0.22}N_{0.006}S_{0.011}{}_{char} + 0.0189H_2 + 0.0137C_4H_6 \quad (12)$$

$$\Delta H = 39.65\ kW \quad \Delta G = 40.22\ kW$$

The units for the energies in equation 12 is kW because the tire feed is assumed to be 1mol/s. In equation 12, it is assumed that the production of NOx, SOx and H_2S are not reported in the gas phase, because there is insufficient oxygen to produce a significant amount of oxygenated gases by pyrolysis, hence their molar composition in the gas phase is much smaller than the hydrocarbon gases. The presence of zinc oxide in tire formulation prevents sulfur-oxidisation. In addition, the quantity of S and N reported in the liquid compounds and the solid phase is much higher than the amounts reported in the gas phase. Therefore, for ease of theoretical calculation, the S and N in the feed are assumed to be transferred only to the liquid and solid phases.

The process as described by equation 12 requires energy input for it to be feasible as indicated by the positive ΔH and ΔG. A positive ΔG across a process indicates the amount of energy equivalent to mechanical work that must be supplied for the process to be feasible (we refer this as the work requirement of the process), while a positive ΔH indicates the total amount of energy to be supplied in the form of heat or work. When the energy is supplied in the form of heat alone (Q = ΔH), as would be the case when a fuel is burnt to produce the energy, the heat must be of the quality, by virtue of temperature, that would match the work requirement (ΔG). Thus, the temperature required for the heat to match the work requirement is referred to as the Carnot temperature.

When supplying energy to the pyrolysis process in equation 12, one seeks to satisfy either ΔH or ΔG depending on which one is limiting. The process is said to be work limited because the value of ΔG is higher than ΔH. Thus, supplying the minimum energy required (ΔH) will not be enough to meet the work requirement even if it is supplied at the highest quality. In order to satisfy the work requirement, high-quality energy must be supplied in excess into the process and then remove the excess energy from the process as low-quality heat. Thus, the amount of fuel to burn should be such that the work required by the pyrolysis process is satisfied. This is equivalent to making ΔG = 0 by adding oxygen as a feed to the overall material balance. Note that by satisfying the work requirement, the process will have excess energy (ΔH is negative) which must be removed in the form of heat. Note that having excess heat means that cooling equipment and utilities will be needed and therefore will increase the running and capital cost of the plant.

The overall material balance for a pyrolysis process with ΔG = 0 when additional tires are burnt is shown in Figure 3.1 and equation P1.

$$1.084CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 0.108O_2 = 0.551CH_{1.35}N_{0.006}S_{0.006} + 0.394CH_{0.215}N_{0.006}S_{0.011} + 0.084CO_2 + 0.001H_2S + 0.046H_2O + 0.0004NH_3 + 0.019H_2 + 0.014C_4H_6 \qquad \text{(P1)}$$

$$\Delta H = -1.74\, kW; \quad \Delta G = 0\, kW$$

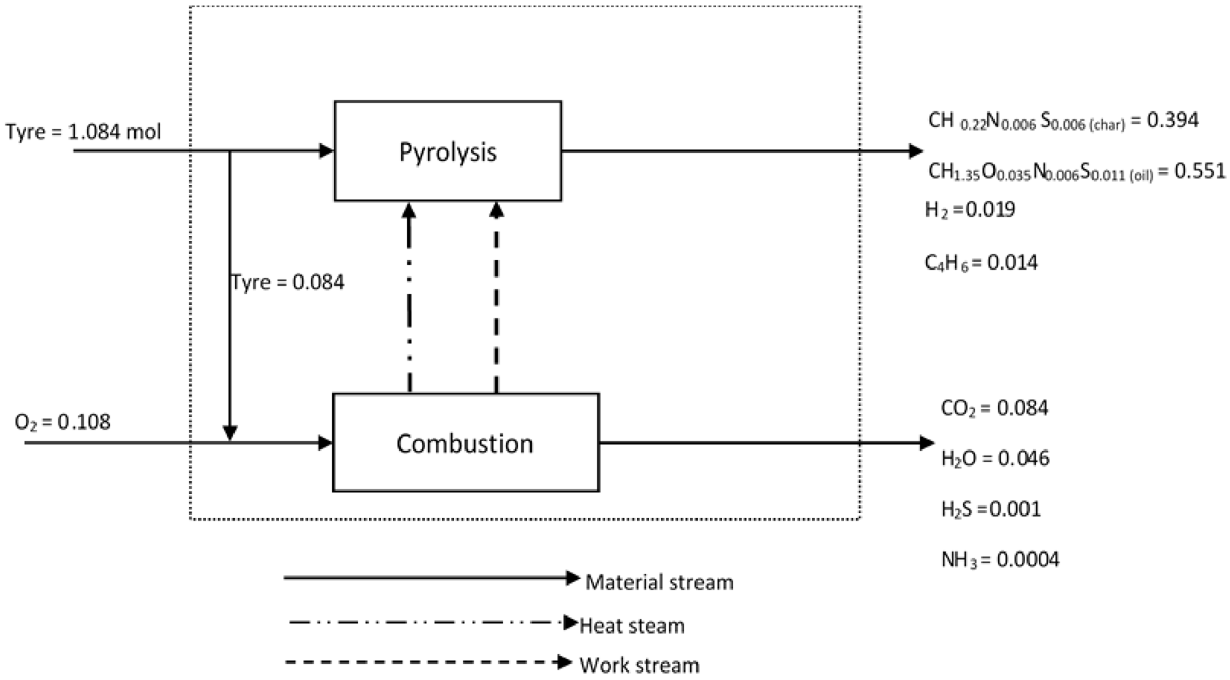

Figure 3.1 Work neutral process (G=0) when additional tires are burnt

The performance is measured of P1 and Figure 3.1 is as follows:

$$Carbon\ Efficiency = 92.23\%$$

$$Atom\ Economy = 75.22\%$$

$$E - factor = 0.336$$

$$Chemical\ potential\ efficiency = \eta_{cp} = 99.72\%$$

Since an additional number of tires are burnt to supply the energy needed, the process produces carbon emissions thus lowering the carbon efficiency to 92%. Equally the atom economy achievable is 75% due to the increase in the feed which does not form the desired products but instead is turned to waste (carbon dioxide etc.). However, despite the small increase in emissions the process conserves the energy potential of the tires, the chemical potential efficiency of the process is almost 100%. This is the biggest indicator that the process has minimal impact on the environment.

Often pyrolysis processes are powered by the off-gas. This presents an alternative strategy for supplying energy requirements. If all the hydrogen and butadiene produced by the system are burned to supply the energy required, the overall system remains work deficient, which means the system won’t happen unless more gas products are needed than what the system currently produces. Therefore, an additional amount of butadiene could be procured to meet the work requirements of the process. Figure 3.2 shows the pyrolysis system using the gas fraction (P2). The overall material balance for tire pyrolysis process that is work neutral is:

$$CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 0.09O_2 + 0.00102C_4H_6 = 0.551CH_{1.35}O_{0.035}N_{0.006}S_{0.006_{oil}} + 0.394CH_{0.22}N_{0.006}S_{0.011_{char}} + 0.059CO_2 + 0.0628H_2O \qquad (P2)$$

$$\Delta H = -2.97\ kW; \quad \Delta G = 0\ kW$$

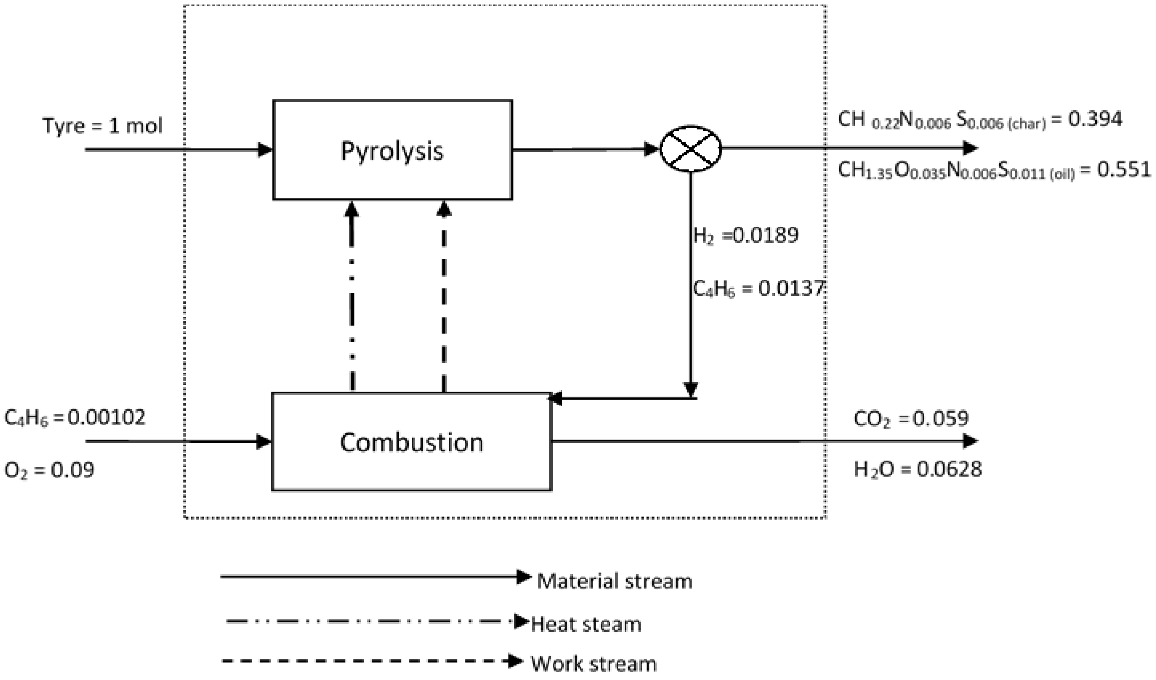

Figure 3.2. Waste tire pyrolysis fueled by producer gas.

If all the products; liquid oil, and char are considered as desired products the performance is measured of P2 is as follows:

$$Carbon\ Efficiency = 94.12\%$$

$$Atom\ Economy = 85.53\%$$

$$E - factor = 0.289$$

$$Chemical\ potential\ efficiency\ (max) = \eta_{cp} = 99.8\%$$

The performance of the pyrolysis improves when the product gas is used to fuel the system. The carbon efficiency increases to 94.12% from 92% (P1) whereas the atom economy increases to 86% and E-factor reduce to 0.289, suggesting that carbon resources are better utilised by burning the product gas compared instead of burning waste tires. In addition, the product gas contains greater LHV per mole than the tire feed, which means less material is being burned overall, thus producing less carbon dioxide emissions.

A further alternative for providing the additional energy to pyrolysis is to burn a portion of the pyrolysis oil (PTO), this is given by the material balance P3:

$$CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 0.093O_2 = 0.478CH_{1.35}N_{0.006}S_{0.006} + 0.394CH_{0.215}N_{0.006}S_{0.011} + 0.073CO_2 + 0.0004H_2S + 0.0004NH_3 + 0.019H_2 + 0.014C_4H_6 + 0.043H_2O \tag{P3}$$

$$\Delta H = -0.88\ kW; \quad \Delta G = 0\ kW$$

$$Carbon\ efficiency = 92.7\%$$

$$Atom\ economy = 76.29\%$$

$$E - factor = 0.32$$

$$\eta_{cp} = 99.1\%$$

The performance of the system decreases when the product oil is burned to supply the required energy. However, the advantage of using the product oil is that unlike the gas system, no additional amount of oil needs to be procured to supplement that which is produced by the system. There is a sufficient amount of oil produced by the system to supply the heat but also a significant amount to be sold as a product.

The next alternative method of energy supply is given by material balance P4, where char is burned to fuel the pyrolysis reactor with the target of a work neutral process:

$$CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 0{,}115O_2 = 0{,}551CH_{1.35}N_{0.006}S_{0.006} + 0.281CH_{0.215}N_{0.006}S_{0.011} + 0.113CO_2 + 0{,}0096H_2S + 0{,}0007NH_3 + 0.019H_2 + 0.014C_4H_6 + 0.005H_2O \tag{P4}$$

$$\Delta H = -1.142\ kW; \quad \Delta G = 0\ kW$$

$$Carbon\ efficiency = 88.7\%$$

$$Atom\ economy = 70.81\%$$

$$E - factor = 0.42$$

$$\eta_{cp} = 98.9\%$$

The carbon efficiency reduces to 89%, the atom economy to 70.8% and the E-factor increases to 0.42. This suggests that char combustion produces more waste by losing 11% of the carbon source. The maximum chemical potential efficiency of the process remains approximately 99% showing that in principle, it is possible to conserve the total chemical potential of the tire in their conversion provided all products are considered as useful products. The process target for both was set at ΔG equal to zero, which in essence means there is no work loss during thermolysis.

The other alternative is to burn liquified petroleum gas (LPG) to fuel the pyrolysis process so that all products could be sold off for profits. The equation P5 describes a case where LPG is burned together with the product gas to provide energy for the process whereas P6 describes a case where all the energy for pyrolysis is supplied by LPG and all the products are considered desirable.

$$CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 0{,}09O_2 + 0.0011C_3H_8 = 0{,}551CH_{1.35}N_{0.006}S_{0.006} + 0.394CH_{0.215}N_{0.006}S_{0.011} + 0.0581CO_2 + 0.0644H_2O \tag{P5}$$

$$\Delta H = -2.998\ kW; \quad \Delta G = 0\ kW$$

$$Carbon\ efficiency = 94.19\%$$

$$Atom\ economy = 78.01\%$$

$$E-factor = 0.29$$

$$\eta_{cp} = 99.42\%$$

$$CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 0{,}0954O_2 + 0.0191C_3H_8 = 0{,}551CH_{1.35}N_{0.006}S_{0.006} + 0.394CH_{0.215}N_{0.006}S_{0.011} + 0.0572CO_2 + 0.019H_2 + 0.014C_4H_6 + 0.0763H_2O \tag{P6}$$

$$\Delta H = -2.67\ kW; \quad \Delta G = 0\ kW$$

$$Carbon\ efficiency = 94.59\%$$

$$Atom\ economy = 78.23\%$$

$$E-factor = 0.29$$

$$\eta_{cp} = 99.44\%$$

The results observed in P5 and P6 suggest that using LPG as fuel leads to a higher carbon efficiency compared to a process using tires (P1), oil (P3) and char (P4) as fuel. However, has the same performance as processes using butadiene in exception to the atom efficiency caused by excess water produced.

Comparing the six pyrolysis processes, the results suggest that using the gaseous products to fuel the pyrolysis process best conserves the carbon resource and generates the least amount of waste. However, the system does not produce enough gaseous products; therefore, an additional supply of 1.3-butadiene or LPG is required. The sustainability of the process would depend on the sale of pyrolysis oil fraction versus the cost of LPG or butadiene.

If the oil is sold without upgrading at the price of heavy fuel oil (0.27$/l), and the char is sold as low-value carbon black at 0.037$/kg, it is estimated that a revenue of $207 per ton of waste tire can be achieved when additional 1.3-butadiene ($1.5/kg) is used to fuel the process and $217 per ton when the processes are solely fuelled by LPG solely. In comparison, the revenue would be 269$/ton of tire if an additional number of tires (P1) is used for energy needs of the pyrolysis process, and the gas is sold at the market price for 1.3-butadiene. The revenue increases to 288$/ton of tire when a fraction of char is burned instead, however, the carbon dioxide emissions for char fuelled pyrolysis process would almost double and would add further complexities to the process depending on the purity of the gas desired. It is necessary to mention that the capital costs are not included in the analysis. Therefore, to conserve the carbon resource, the gaseous product must fuel the pyrolysis process.

3.3.2 Conversion of tires to liquid fuels via Gasification route

The process systems presented in this section involve the gasification of tires to syngas, which can be converted to various liquid fuels and chemicals. Through gasification, the produced syngas can be cleaned of toxic gases providing environmentally friendly beneficiation of waste tires. Various liquid hydrocarbons can be produced from syngas, via the Fischer-Tropsch reactor (FT synthesis). Commonly the FT synthesis reactor does not produce a single set of products but rather a huge spectrum of products made up of paraffins and olefins. In order to have a favourable comparison with the pyrolysis process, three sets of representative products are required. The product composition and selectivity are influenced by the chain growth probability α. When using supported ruthenium (Ru) as FT synthesis catalyst, a chain growth probability of 0.9 is achieved to achieve a yield of diesel fraction higher than 71 wt.%. To generate the material balance for the FT reactor, the diesel fraction will be represented by hexadecane, the wax fraction will be represented by triacontane and the gases will be represented by methane since in comprises a high composition of the C1-C5 components.

As mentioned, the process starts with the gasification of tires with steam to produce syngas. Steam is selected as the gasification agents since it yields a higher composition of H_2/CO compared to oxygen. The material balance for syngas production using steam is given by the material balance:

$$CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 0.98H_2O = CO + 1.44H_2 + 0{,}007H_2S + 0{,}005NH_3$$

$$\Delta H = 228.984\, kW, \qquad \Delta G = 142.635\, kW$$

It assumed that all the available sulfur leaves as hydrogen sulphide, since chemicals in the tire rubber, such as zinc oxides, prevent sulfur-oxidation [20]. The syngas from gasification is cleaned of acid gases and converted to liquid fuels in an FT unit.

The material balance for the FT reactor unit to is:

$$CO + 2.13H_2 = 0.125CH_4 + 0.045C_{16}H_{34} + 0.0051C_{30}H_{62} + H_2O$$

$$\Delta H = -159.18\, kW, \qquad \Delta G = -74.29\, kW$$

According to the equation, the required ratio of hydrogen-to-carbon monoxide is 2.13: 1 and this implies the inclusion of the water-gas shift reaction, to shift the hydrogen-to-carbon monoxide ratio from the gasification unit. Therefore, the material balance across the water gas shift reactor is:

$$0.22CO + 0.22H_2O = 0.22CO_2 + 0.22H_2$$

$$\Delta H = -9.062\, kW, \qquad \Delta G = -6.28\, kW$$

From the outlined steps, the gasification step requires energy, whereas the water gas shift and the FT-synthesis step are exothermic, thus integrating them with the gasification step would decrease the need to supply energy externally. However, it must be mentioned that the gasification step operates at higher temperatures than the other steps, this essentially means that the energy would have to move against a temperature gradient and practically that might require expensive equipment. A series of heat pumps may be used to achieve this. The overall material balance for a hypothetical fully integrated process is:

$$CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 0.421H_2O$$
$$= 0.097CH_4 + 0.035C_{16}H_{34} + 0.004C_{30}H_{62} + 0.22CO_2 + 0.007H_2S + 0.005NH_3$$

$$\Delta H = 65.07\ kW, \qquad \Delta G = 59.14\ kW$$

The above equation shows that the system still requires energy for it to be feasible. The energy can be supplied by burning additional feed or some of the products. Since the enthalpy is greater than the Gibbs free energy, it means that the process can operate adiabatically and will produce excess work potential, and this leads to process irreversibility.

Figure 3.3 shows the overall process of producing petroleum products when additional number of tires are burned. Therefore, the overall material balance for hypothetical full integrated process to produce liquid fuels when additional tires are burned to supply the energy needed:

$$1.140CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 0.17O_2 + 0.356H_2O$$
$$= 0.097CH_4 + 0.035C_{16}H_{34} + 0.004C_{30}H_{62} + 0.36CO_2 + 0.008H_2S + 0.006NH_3 \tag{G1}$$

$$\Delta H = 0\ kW, \qquad \Delta G = -4.59\ kW$$

The performance of this process equation G1 is as follows:

$$Carbon\ efficiency = 68.4\%$$

$$Atom\ economy = 41.09\%$$

$$E - factor = 1.45$$

$$\eta_{cp} = 99.25\%$$

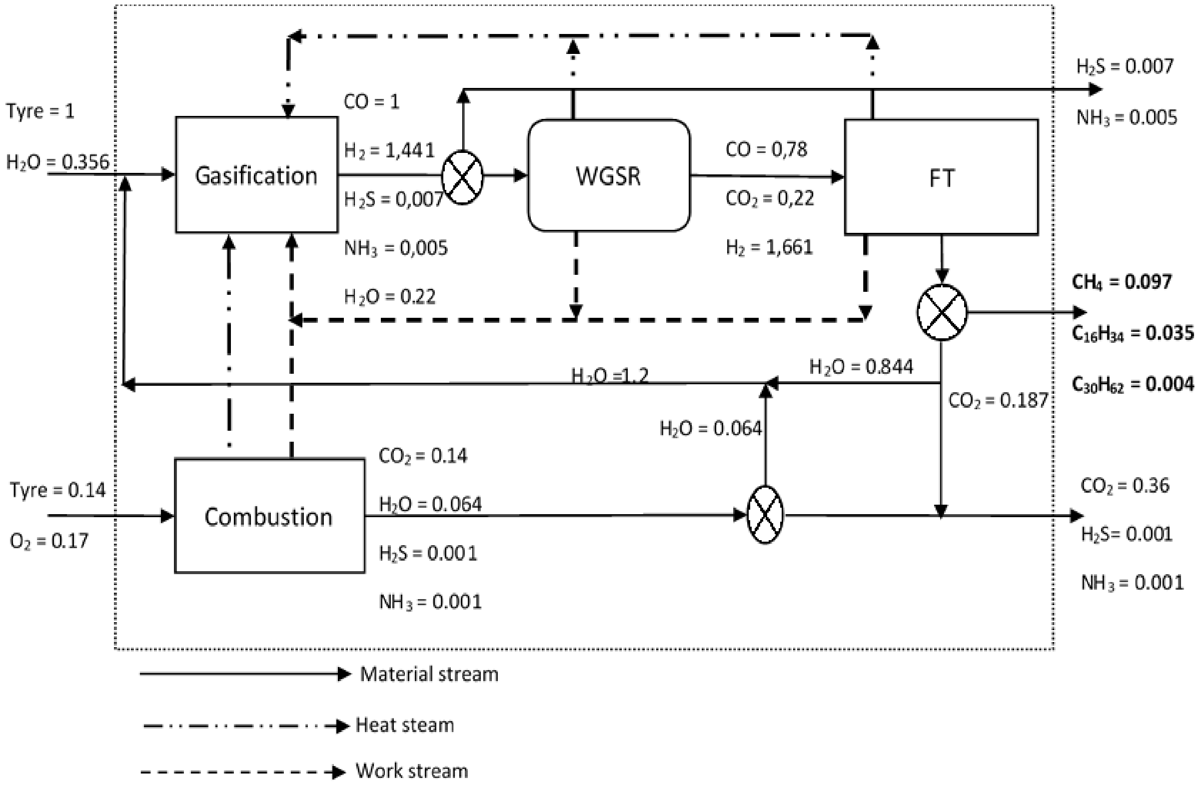

Figure 3.3: Process flowsheet (G1) for the gasification process producing liquid fuels where the energy for gasification is supplied by combustion of a portion of the tire feed.

The performance of G1 shows that the gasification route that uses tires as fuel produces 3 times the amount of carbon emissions compared to the pyrolysis process that uses tires as fuel (P1). The advantage of gasification is that the liquid fuels produced do not contain sulphur and thus could potentially make the gasification route more profitable than the pyrolysis route. Despite the lower carbon efficiency and higher e-factor, the gasification route also conserves the chemical potential on the original feed.

Since the products contain higher heat value than the tires, the carbon emissions of the gasification route can be lowered by burning some of the products to provide the energy needed for the process. G2 shows the overall material balance of a full integrated process and when the gas fraction represented by methane is burned to supply the energy to the system.

$$
\begin{aligned}
CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 0.146O_2 + 0.274H_2O \\
= 0.024CH_4 + 0.035C_{16}H_{34} + 0.004C_{30}H_{62} + 0.293CO_2 + 0.007H_2S \\
+ 0.005NH_3
\end{aligned}
\tag{G2}
$$

$$\Delta H \ = 0\ kW, \qquad \Delta G \ = \ -0.65\ kW$$

$$Carbon\ efficiency \ = \ 70.7\%$$

$$Atom\ economy \ = \ 48.3\%$$

$$E - factor \ = 1.32$$

$$\eta_{cp} = 99.99\%$$

The performance of observed in G2 shows that by using the gas fraction methane as a fuel reduces the impact to the environment, carbon efficiency increases by over 3%, the atom efficiency increases from 41% for tires to 48% for methane. Also, methane fuelled process (G2) produces less excess work compared to G1, which means the process nearly achieved a chemical potential efficiency of 100%. Therefore, using methane is better than using an additional quantity of waste tires.

The oil fraction can also be used instead of methane and tires. G3 shows the overall material balance of a full integrated process and when the oil fraction represented by hexadecane is burned to supply the energy to the system.

$$\begin{aligned} CH_{0.95}O_{0.02}N_{0.005}S_{0.007} \ + \ 0.15O_2 + 0.317H_2O \\ = 0.097CH_4 + \ 0.029C_{16}H_{34} \ + \ 0.004C_{30}H_{62} + 0.318CO_2 + 0.007H_2S \\ + 0.005NH_3 \end{aligned} \tag{G3}$$

$$\Delta H \ = 0\ kW, \qquad \Delta G \ = \ -4.6\ kW$$

$$Carbon\ efficiency \ = \ 68.2\%$$

$$Atom\ economy \ = \ 40.9\%$$

$$E - factor \ = 1.46$$

$$\eta_{cp} = 99.39\%$$

G3 consumes more water and oxygen and produces more carbon dioxide compared to G2, this leads to a lower carbon efficiency and lower atom efficiency for oil compared to gas. However, the performance of the oil is slightly Improved when compared to tires (G1). This result like with the pyrolysis process suggests that fuelling the system with the product gas will have a lesser impact on the environment.

As previously mentioned, material balances in G1-G3 are hypothetical balances and may not be achievable in practice, due to the temperature gradient of the units. More commonly, only the gasification unit can be operated adiabatically whilst all other units release their heat to the environment or other means such as steam cycles which attempt to recover this excess energy through shaft work. Therefore, the overall material balance of the system changes when only the gasification step is operated adiabatically.

Since full integration case has some significant thermodynamic challenges, the following assessments G4-G6 evaluates scenarios where only the gasification adiabatic, this will be called partial integration. Figure 3.4 shows the process diagram when only the gasification unit is heat and work integrated. G4 is the overall material balance when additional tires are burned to operate the gasification step adiabatically:

$$\begin{aligned} 1.492CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 0.6O_2 + 0.194H_2O \\ = 0.097CH_4 + 0.035C_{16}H_{34} + 0.004C_{30}H_{62} + 0.712CO_2 + 0.010H_2S \\ + 0.0075NH_3 \end{aligned} \tag{G4}$$

$$\Delta H = -163.94\,kW, \qquad \Delta G = -165.16\,kW$$

$$Carbon\ efficiency = 52.31\%$$

$$Atom\ economy = 26.14\%$$

$$E-factor = 2.83$$

$$\eta_{cp} = 75.83\%$$

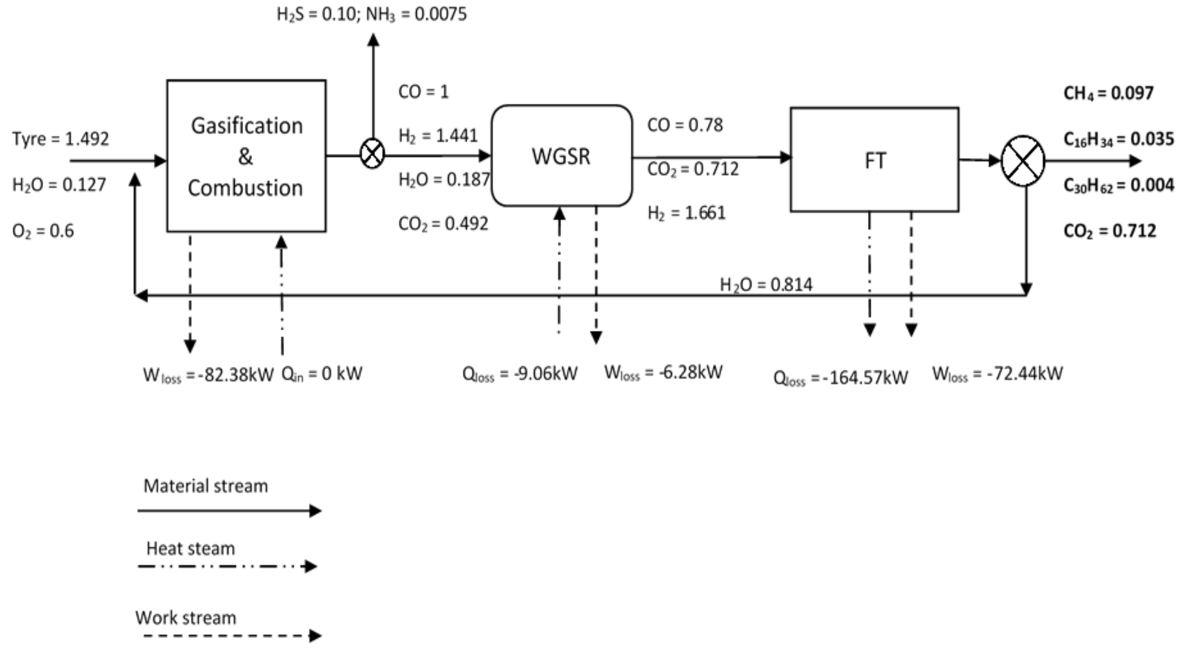

Figure 3.4. Process diagram when additional tires are burned to operate the gasification step adiabatically

Since the process described in G4 is partially integrated the overall system is exothermic and spontaneous. Figure 3.4 shows that the energy potential of the process is lost to the environment, as a result, the chemical potential efficiency reduces from 99.2% (G1) to 75.83%. The carbon efficiency is 52.31%, which means almost 48 % of the carbon resource is lost as carbon dioxide. and the E-factor doubles, while the atom economy is halved, which means increased environmental impact as the process releases more waste and heat to the environment. Therefore, partial integration produces more waste. The other strategy to lower the environmental impact of the partially integrated process pathway is to use part of the product as a fuel source.

The material balance for partial integration using methane as fuel is shown in G5.

$$\begin{aligned} CH_{0.95}O_{0.02}N_{0.005}S_{0.007} \ + \ 0.504O_2 + 0.155CH_4 \\ = 0.035C_{16}H_{34} \ + \ 0.004C_{30}H_{62} + 0.473CO_2 + 0.010\,H_2S \ + 0.0075\,NH_3 \\ + 0.094H_2O \end{aligned} \tag{G5}$$

$$\Delta H \ = -160.17\,kW, \qquad \Delta G \ = \ -147.76\,kW$$

$$Carbon\,efficiency \ = \ 59.1\%$$

$$Atom\ economy\ =\ 29.95\%$$

$$E-factor\ =2.20$$

$$\eta_{cp}=74.67\%$$

Like G4 the above system described by G5 is exothermic and spontaneous owing to a partial integration. Also as seen before with pyrolysis using gas as fuel improves the carbon efficiency and of the process. However, the material balance shows methane as feed to the system, this means the system is not producing enough methane to cover the energy requirements, therefore, an additional amount of methane is needed to drive the process. This will affect the profitability of this process and the oil needs to be sold at a higher value ($0.98/l) compared to the pyrolysis oil which is sold at $0.27/l. the last section of this work will evaluate all the cases.

The last approach is to a fraction of oil product as fuel. The material balance for partial integration using oil is:

$$\begin{aligned} CH_{0.95}O_{0.02}N_{0.005}S_{0.007}\ +\ 0.506O_2\ +0.07H_2O \\ =0.097CH_4+0.015C_{16}H_{34}\ +\ 0.004C_{30}H_{62}+0.55CO_2+0.010\ H_2S \\ +0.0075\ NH_3 \end{aligned}$$

(G6)

$$\Delta H\ =-160.17\ kW,\qquad \Delta G\ =\ -147.76\ kW$$

$$Carbon\ efficiency\ =\ 45\%$$

$$Atom\ economy\ =\ 21.10\%$$

$$E-factor\ =3.76$$

$$\eta_{cp}=66.30\%$$

Therefore, the oil fraction has a higher impact to the environment than both gas and tires since its overall carbon efficiency is 45% which is less than that of tire (G4) at 52% and gas (G5) at 59%. The E-factor for oil (G6) is 3.76 well above the average 2.5 achieved by the other systems. However, the advantage of this process (G6) is that it produces enough oil to cover the energy requirements and have enough oil left to sell as a product. Since the diesel produced by FT process is predominantly alkanes it has the potential to be sold at higher value that the oil obtained via pyrolysis. This, therefore, puts this process at an advantage in terms of profitability, as will be shown later.

The process described in G4 – G6 produce excess energy and if not recovered would mean that the gasification process fails to meet the energy efficiency values achieved by the pyrolysis process. To reach the same energy efficiency achieved by pyrolysis it is necessary to recover the excess Gibbs free energy as electricity. Let us consider the process described in G4. In this system, only the gasification step is operated adiabatically whilst other units release their energies to the environment. Simple heat engines are applied to the water-gas shift unit and FT unit as shown in Figure 3.5. The heat engines are assumed to operate at the Carnot temperature of the units. The Carnot temperature is the single temperature at which heat can only be used to satisfy the work requirements of a process and such a process will not lose or take additional energy to the environment, in that it will reversible [14,21]. Figure 3.5 shows the process (G7) which applies the notion of heat engines to produce electricity. The chemical potential efficiency of the process increases to 86.76% when 78.72 kJ/mol (4GJ/ton) of electricity is produced. Therefore, producing electricity gives the gasification routes more profitability than pyrolysis, which has no capacity for power generation.

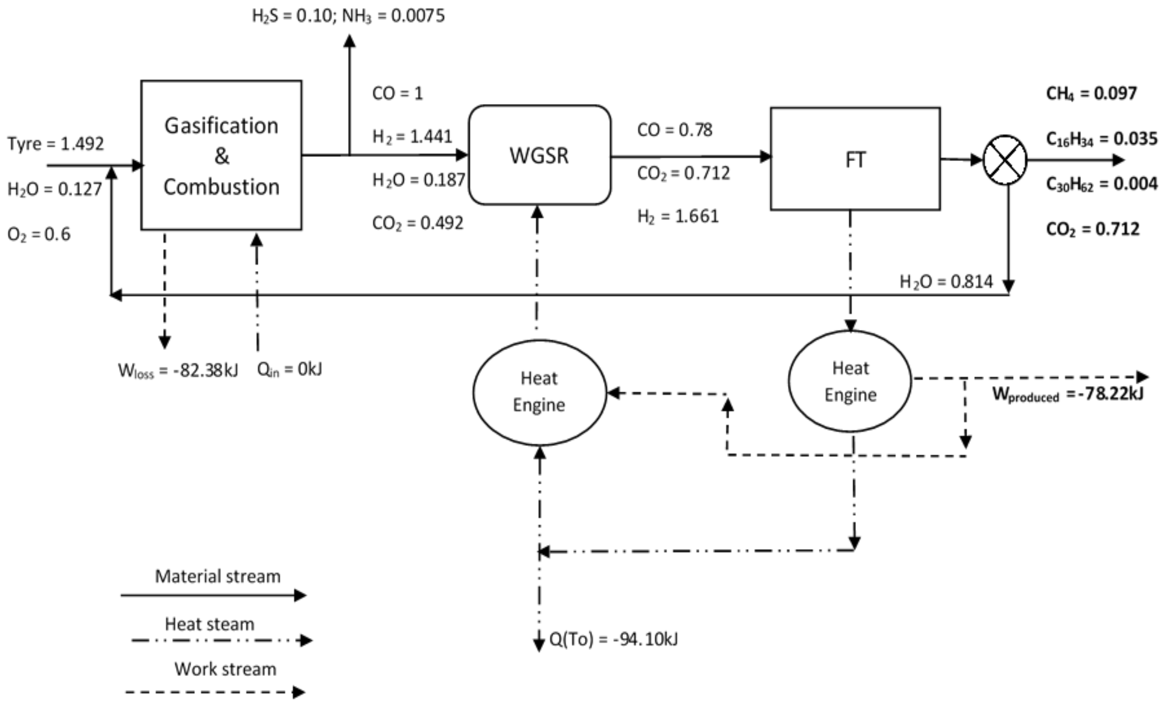

Figure 3.5. Process flowsheet (G7) for the gasification process producing liquid fuels and electricity production

When electricity is sold at \$ 0.098/kWh and the liquid fuel is sold as diesel at \$ 1.01/l [22], the process in G7 (Figure 3.5) has the potential to generate revenue of \$ 666/ton of the tire, three times that of pyrolysis (\$287/ton). Gasification provides a higher revenue than pyrolysis but requires more capital investment due to the different units required to achieve the required product.

3.3.3 Comparison of pyrolysis route and gasification

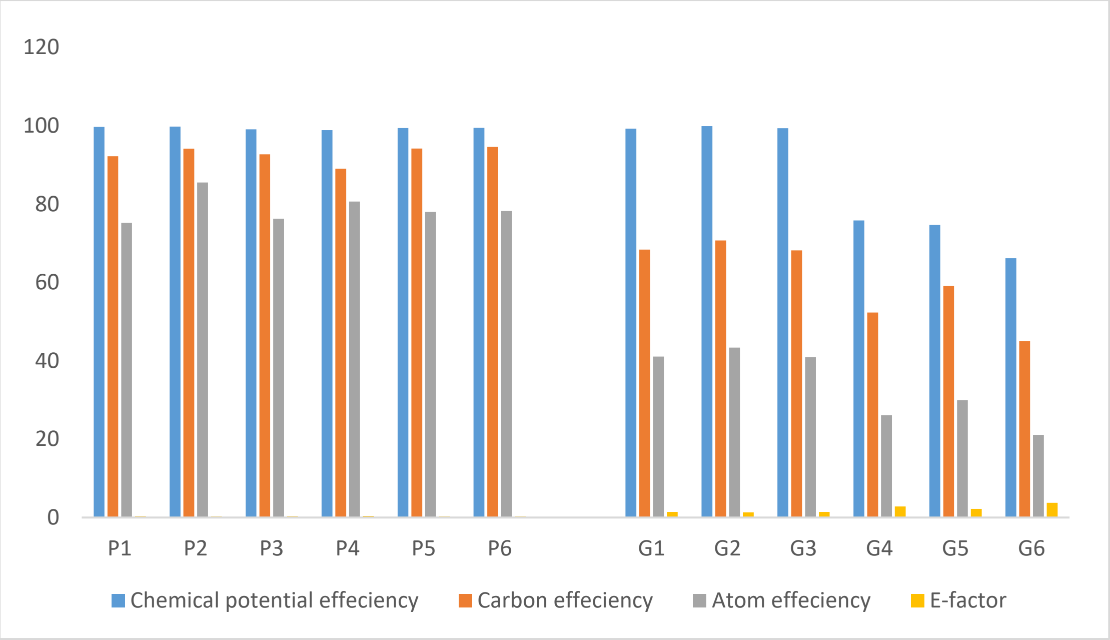

Figure 3.6. Comparison of process routes for water tire recovery

Figure 3.6 shows that the pyrolysis systems perform far better than the gasification systems in terms of the overall carbon efficiency and chemical potential efficiency. However, this comparison considers an ideal case whereby all three fractions produced by pyrolysis system are considered desirable. If the oil fraction is considered the only desired product, then the carbon efficiency for pyrolysis system decreases to 54.9% and the chemical potential efficiency to 60.4%, similar to the gasification routes. Considering that the oil product from pyrolysis is heterogenous with a sulphur content above the standard for commercial diesel fuel, the difficulties involved in desulphurizing liquid fuels make gasification a better route for the production of liquid fuels. For gasification systems, the production of electricity utilises the waste tire carbon resource more efficiently and generates the least amount of waste. The chemical potential efficiency for the FT process with electricity production (G7) is higher than all other partial integration gasification systems. The advantage of gasification over pyrolysis is the purity of products achieved. The liquid fuels achieved through FT-synthesis are higher grade fuels compared to those of pyrolysis which contain high levels of sulphur and PAH’s, and therefore, gasification has the potential to make a more significant profit margin than pyrolysis.

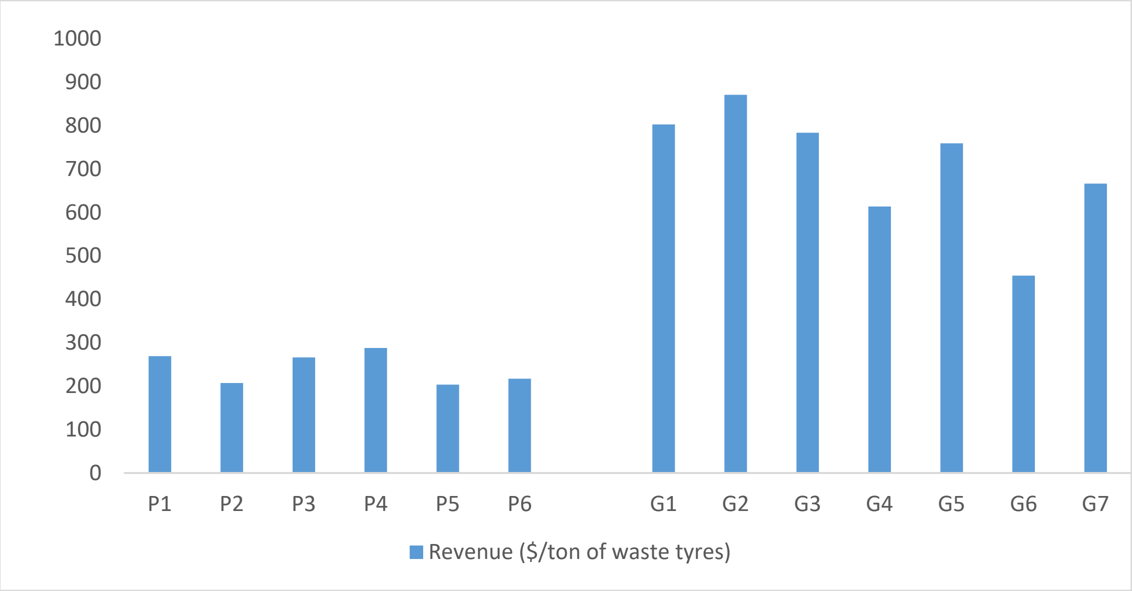

Figure 3.7. Comparison of revenue generated by the processes

Figure 3.7 shows that gasification process routes have a higher revenue generation that the pyrolysis processes. For example, the revenue achieved for the G7 process when liquid fuel product and electricity are sold is $666 per ton of waste tire approximately three time the revenue generated by the most efficient pyrolysis process. However, the gasification route requires both significant capital investment and more skilled operators compared to pyrolysis. The emissions of the gasification route are much higher, but there is a market for these process products unlike pyrolysis, whose products are often considered low value, which affects the economic feasibility of pyrolysis.

3.4 Conclusion

In this work, the fundamental thermodynamic analysis was used to compare two technologies to convert waste tires to useful products by determining the performance limits of various idealized process pathways. The comparison was based on carbon efficiency and exergy efficiency or chemical potential efficiency. This comparison looks at how much of the carbon in the tire is transferred to the useful products and how much of the energy content in the tire has been transferred to the product which indicates the potential impact to the environment of each process. Both processes are viable for eliminating this hazardous waste and converting it into useful products. However, thermodynamically the pyrolysis process performed better than the gasification route with a higher overall carbon efficiency and chemical potential efficiency, meaning that the pyrolysis process conserves the carbon resource and has minimal impact to the environment. Most notably the gasification route loses about 45% of the carbon feed to carbon dioxide, therefore, to make the processes more environmentally friendly a carbon capture system would need to be installed, however this further increases the overall capital cost for the gasification route. Comparing the two process flowsheets, pyrolysis is simpler to build and operate.

However, the pyrolysis route has observed drawbacks in its product quality, which is substandard compared to commercial products (i.e. transportation fuels and carbon black). The char produced by the pyrolysis process is a heterogeneous material with regards to the ash content, particle size, absorption properties, structure and both surface chemistry and activity and the liquid fuels have a high content of nitrogen and sulphur compounds which affects the economic feasibility of pyrolysis. Substantial refining is therefore required for all the pyrolysis products, whereas the gasification route produces products that meet the requirements from the start. The gasification route also offers the highest revenue per ton of waste tires at $666 per ton of waste tire compared to $287 per ton achievable by the pyrolysis process.

With gasification profit margins potentially being three times better than pyrolysis, it becomes difficult to recommend pyrolysis of waste tires - despite the better environmental performance. It would appear that commercial pyrolysis processes will always suffer from financial difficulties due to the fact that “off-take” agreements will be difficult to secure for low-quality products that are difficult to refine. Moreover, legislation on fuel quality and emissions is becoming increasingly stringent, calling into question the long-term viability of pyrolysis processes where it is not possible to effectively eliminate sulphur and other contaminants.

The work done on this paper shows that from an environmental standpoint, converting waste tires to transportation fuels is preferable to landfill and that gasification processes could be argued to offer better long-term prospects, despite their higher emissions than pyrolysis. Fossil fuels are already being burned all over the world, and it has been shown that waste tires could provide similar or better performance than existing fossil fuel processes, so there is still be a strong environmental case for the use of waste tires in gasification.

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4 Syngas production from CO2-assisted gasification of waste tires: effect of spent FCC catalyst

Manuscript

Title: Effect of Spent Fluid Catalytic Cracking (FCC) Catalyst on Syngas Production from Pyrolysis and CO_2-assisted Gasification of Waste Tires

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Short summary

In the previous chapter, it was concluded through theoretical means that the gasification route was the best thermochemical conversion option for waste tires. However, theoretical means are often, far from real applications since in the equilibrium calculations the ideal state is adopted, whereas real gasification reactions are always limited by the reaction kinetics, mass transport, unknown reactions, and interfaces. Also, in the review chapter, it was shown that the co-gasification of waste tires was more effective in ensuring complete devolution and material recovery. In this chapter, we evaluate the effect of adding spent fluid cracking catalysts (FCC) from the petroleum industry to pyrolysis and CO_2-assisted gasification of waste tires. We also investigate the effect of temperature and catalyst position (in-situ and quasi-in-situ) during CO_2-gasification of waste tires only. Tires produce a vast amount of tars and char. Catalysts have long been used for the thermal cracking of tars to syngas but the cost of catalyst as well as regeneration is high, making catalytic pyrolysis and gasification unattractive. A spent fluid cracking catalyst is a waste product from the hydro-refining, hydro-cracking, and catalytic reforming processes of the petroleum industry. Due to its content of heavy metal impurities, FCC is regarded as hazardous waste. However, the presence of metallic oxides which act as reaction catalysts elsewhere makes the FCC a great candidate to use in pyrolysis and gasification. When compared to other methods, the CO_2 catalytic gasification increased the overall syngas yield by 81.25% compared to non-catalytic gasification, by 205.5% compared to non-catalytic pyrolysis and by 44.7% compared to catalytic pyrolysis.

Declaration by canditate:

The scope of my contribution to the chapter is as follows:

Planning of experiments	90%
Conducting the experiments	90%
Results interpretation	70%
Compilation of chapter	100%

The following co-authors have contributed to this chapter as per following:

Co-author	Nature of contribution		Contact and signature
Kiran Burra	Results interpretation	30%	Email:
	Revision of manuscript	50%	
Howard	Conducting experiments	10%	Email:
Ashwani Gupta	Revisions of manuscript	50%	Email:

I declare that the above information is true and reflects the nature and extent of the contributions of the candidate and the co-authors

Signature of candidate:…………………….. Date:…………………….

Effect of Spent Fluid Catalytic Cracking (FCC) Catalyst on Syngas Production from Pyrolysis and CO_2-assisted Gasification of Waste Tires

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Abstract

With growing demands for improved energy recovery from waste tires, incorporating waste catalysts from different sectors can provide a synergistic solution. This paper investigates the effect of using spent fluid catalytic cracking (FCC) catalyst on evolutionary behavior and yield of syngas (CO, H_2, and light hydrocarbons), and char and energy yields during pyrolysis and CO_2-assisted gasification of waste tires at 900 °C in a fixed-bed semi-batch reactor. The effect of catalyst position (in-situ and quasi-in-situ catalytic modes) and the temperature were also examined during catalytic CO_2-assisted gasification for energy and chemicals production. The results reveal that the presence of spent FCC catalyst resulted in higher syngas and energy yields. The CO_2-assisted gasification provided CO-rich syngas with higher yields than pyrolysis. The quasi-in-situ gasification provided increased syngas and energy yields by 24% and 23% respectively, as compared to in-situ catalytic gasification, which revealed that quasi-in-situ catalytic gasification to be more efficient and effective for increased syngas yields. Increasing the temperature to 950 °C increased the yields syngas and energy owing to improved reforming and cracking reactions. This viability of utilizing spent FCC catalyst offers improved waste management economics for FCC plants while simultaneously improving the energy recovery from waste tires.

4.1 Introduction

The amount of waste tires produced worldwide is growing rapidly and it falls under the category of materials that are difficult to recycle [1,2]. Their decomposition behavior is caused by the different polymers that make up tires. The volatile matter in tires is contributed by mainly styrene-butadiene rubber (SBR), butadiene rubber (BR), and natural rubber (NR) present in the tires. To give the tire its unique properties of heat resistance, durability, glass transition temperature, modulus, and elongation break, the polymers are cross-linked with sulfur in a process called vulcanization [1]. Cross-linking binds together all the polymer chains at multiple points, producing, in principle, one giant covalently bonded molecule commonly called a polymer network characterized by non-reversible sulfur crosslinks.

Each polymer chain behaves differently and yields different products under the same operating conditions. The choice of operating conditions is critical in forming the desired product. The operating conditions are linked to the heat capacity, kinetic parameters, enthalpy, and thermal diffusivity of the species involved [2]. Several studies have shown the potential of pyrolysis to recover valuable material from the waste tires [3–7]. Waste tire pyrolysis produces products in all three phases (char, liquid, and gas/syngas) that can be used as fuel or chemicals in many industrial applications. The liquid phase or tire pyrolytic oil (TPO) is a complex mixture of aromatic hydrocarbons, n-paraffin and olefins terpenes, mono and poly aromatics, nitrogen and sulfur containing heterocycles and oxygenates [8,9]. The oil can be upgraded for use as a fuel. Char is a combination of carbon black, zinc, sulfur, silica, and clay. The gas phase is predominantly a mixture of non-condensable light hydrocarbons (C_1-C_5), H_2, CO_x, and sulfur compounds (SO_x and H_2S), which is utilized as fuel gas to fire the pyrolysis furnace. The yield of each phase depends on the operating conditions such as temperature, heating rate, residence time and tire composition.

Pyrolysis process can be categorized according to slow and fast pyrolysis. Pyrolysis reactors are thus grouped according to these categories. Fixed bed, both batch and semi-batch reactors, rotary ovens, auger reactors and stirred tank reactors, are associated with slow pyrolysis as these reactors are often operated at low temperatures and low heating rates and long residence time for both solid and vapor products formed. Fast pyrolysis reactors include fluidized bed reactors (bubbling and circulating), rotary kilns, spouted reactors and ablative reactors. These reactors perform the pyrolysis process with very short residence time and temperatures up to 600-800°C. Taleb et al. [10] used a fixed bed reactor to study the thermal behavior of pyrolysis products. Their results concluded that the optimized liquid oil yield of 32% is achieved at 500ºC, and the liquid product consists of high contents aromatic compounds such as benzene, toluene, xylene, and limonene, as well as a complex mixture of C5- C16 organic compounds. Al-Salem [11] also used a fixed bed reactor and achieved a maximum liquid yield of 48% at 500 ºC. These authors used a much lower inert gas flow of 20 mL/min than the 5 L/min used by [10] and this may have contributed to the difference in the product yield since a lower inert gas flow may allow enough time for the larger gas compounds to condense.

A study by [12], showed that when using a rotary reactor the maximum yield of liquid oil was 44 wt.% at the pyrolysis temperature of 550 ºC. The high heating value of this liquid was 39.3 MJ/kg with a specific gravity of 0.95. The liquid oil was analyzed, that showed it contained about 14% light naphtha, 4% heavy naphtha, and 36% middle distillate, respectively. The other 46% was a liquid with a boiling point above 350 ºC. A further FTIR analysis revealed that the liquid contained undesired compounds with sulfur and nitrogen functionalities, which may suggest that the liquid oil is not suitable for direct application as a diesel fuel without further purification. Bowles et al [13] also used a rotary kiln reactor and found that the maximum oil yield of 38.4 ± 0.9% at 550 ◦C. This oil contained 4.5 ± 0.1 wt.% limonene.

Muelas et al. [14] studied the combustion behavior of pyrolysis oil obtained from a continuous auger reactor using a drop tube facility. The behavior of the pyrolysis oil was compared to conventional heating oil. The pyrolysis oil was found to have considerably lower burning rates, smaller flames and a higher propensity to soot formation. The pyrolysis process performed better thermodynamically than the gasification route, with a higher overall carbon efficiency and chemical potential efficiency, implying that the pyrolysis process conserves the carbon resource and has a low environmental impact [15].

Despite these concentrated efforts, several companies involved in waste tire pyrolysis are closing due to difficulty in finding a market for the liquid and solid products because of their poor quality. This is the reason that complete conversion of the tire to syngas is preferable since the gas can be either combusted or converted to valuable materials. However, the production of tar, non-condensable hydrocarbons, and char persist which lowers the yield of syngas. Tar is the most difficult of these byproducts to remove from syngas. [16]. To overcome this challenge, high temperature, and catalyst gasification can be used to aid the thermal cracking of large hydrocarbons and also promote the reactivity of char. Ongen et al. [17] used a fixed bed reactor to study the gasification of waste tires in air or oxygen atmospheres. The highest yield of syngas (41 wt.%) was obtained at a gasification temperature of 800 °C under air atmosphere. When gasification was combined with the pyrolysis step, the syngas yield improved to 42.6 wt.%. Under these conditions, the syngas contained 40 v/v% methane and 34 v/v% hydrogen with a high heating value of 20.5 MJ/m^3. Karatas et al. [18] compared the results obtained from a fixed bed gasifier to a bubbling fluidized gasifier. Their study showed that the fluidized bed gasifier achieved a higher gas yield, gas LHV and syngas efficiency when compared to a fixed bed gasifier. Their study also investigated the effect of equivalence ratio (ER) and temperature on syngas product. The study showed that lower ER values resulted in lower concentrations of CO_2, higher concentrations of H_2 and CH_4 and higher LHVs. However, lower ERs increased the formation of polyaromatic hydrocarbons and reduced the bed temperature. ER between 0.29-0.60 are therefore recommended to keep the bed temperature above 700 °C. The LHV of the product gas ranged from 2.66-7.03 MJ/Nm^3 in this ER range, decreasing with an increase in ER.

Zang et al. [19] achieved a similar LHV of 2.8-7.4 MJ/Nm^3 when ER was varied from 0.22 to 0.55 in a fluidized gasifier. Karatas et al. [18], used a bubbling fluidized bed gasifier and showed that increase in the air feed (to change the equivalence ratio, ER), reduced the syngas quality. The concentrations of CO and CO_2, CH_4 and H_2 yields increased with decrease in ER. The H_2 composition in the syngas decreased from 20.01% to 5.05% when the ER was increased from 0.15 to 0.45. Similar thermal behavior was observed in Ongen et al. [17]. This in turn had a negative impact on the LHV of the product gases as well as the cold gas efficiency of the gasifier. However, Mavukwana et al. [15] showed that lower ER values results in lower bed temperature, which reduces the yield of gas. Steam addition at higher ER was shown to improve the LHV and quality of the syngas. The optimum ER was shown to be 0.33. Serrano et al. [20], using a bubbling fluidized reactor showed that the LHV reduces from 8.2 MJ/Nm3 to 5.3 MJ/Nm3 when ER is increased from ER = 0.16 to ER = 0.33. The carbon conversion and LHV increased by 7.2% and 0.75 MJ/Nm^3, respectively with increase in temperature from 700 to 850 °C. Several numerical and experimental studies have shown that steam gasification represents the best choice for the utilization of waste tires [21–23].

Donatelli et al. [23], using a rotary kiln, showed that the energy content of the product gas is affected by the steam to waste tire feed ratio (FR). Increase in the steam feed ratio, provided favorable reforming reactions, which improved the quality of the syngas. Detailed studies on parameters affecting the gasification of waste tires are found in [18,24,25]. These researchers concluded that the choice of the gasification agent depends on the desired quality of the syngas, ratio of H_2/CO, LHV of the gas, the concentration of tar, and the yield of char. Steam produces a higher concentration of H_2 and CH_4, which lead to higher LHV of the syngas. However, steam gasification is an endothermic process, and more heat is required to maintain the desired gasification temperature. It is therefore recommended that the quantity of steam used should not exceed the stoichiometry requirements to reduce the energy required and maximize the LHV of the product gas.

Catalysts have provided a special means of reducing the product spectrum and targeting specific products. Catalysts such as γ-Al_2O_3 (Ni-based, and iron-based), zeolites, dolomite, MgO, and CaO calcined in dolomite, biomass char, $CaCO_3$ have been explored to reduce the amount of tar during waste tire gasification and pyrolysis to improve syngas production [7,16,26–31]. The studies reported by Elbaba et al. [28] showed that hydrogen yield increased from 0.68 to 5.43 wt. % in the presence of Ni−Mg−Al catalyst during steam assisted gasification of waste tires. Zhang et al. [32] investigated the influence of Co/Al_2O_3, Cu/Al_2O_3, Fe/Al_2O_3, and Ni/Al_2O_3 on hydrogen yield and carbon nanotube production. Ni/Al_2O_3 catalyst produced the highest yield of H_2, as well as nanotubes compared to other catalysts which were hindered by the excessive formation of amorphous-type carbon on the surface of the catalyst.

Yu et al. [33] investigated the influence of Fe_2O_3 catalysts on the evolution mechanism of gas products from catalytic pyrolysis of tire rubber. The presence of Fe_2O_3 increased the proportion of CH_4 and H_2, while it reduced the proportion of $CH_2{=}CH_2$. Alsurakji et al. [34] demonstrated that the synergistic effect of NiO and MgO nanoparticles (SBNs) during catalytic pyrolysis of waste tires was extremely effective in lowering the operating temperature and speeding up the pyrolysis reaction. Kordoghli et al. [35] used powdered catalyst (MgO and $CaCO_3$), acid (zeolite ZSM-5) and neutral (Al_2O_3) catalysts supported on oyster shells to determine their influence on the composition of the pyrolysis gases. Their results showed that Al_2O_3/Oyster shell (OS) increased the gas fraction as well as the amount of gel deposited on the catalytic bed. MgO/OS provided the highest concentrations of hydrogen and hydrocarbon species. Due to the low temperature, $CaCO_3$/OS and ZSM-5/OS only achieved modest results. Biomass ash was also found to provide significant catalytic effect than fly ash during CO_2 gasification of tire char [36].

Steel slag (SS) was used as a catalyst in catalytic pyrolysis of waste tires in CO_2 atmosphere by Cho et al. [31]. At low temperatures, the effectiveness of CO_2 on pyrolysis of waste tires was increased by nearly 400% in the presence of SS. However, there is a disadvantage associated with direct catalyst addition, which provides high propensity for the formation and accumulation of coke on the catalyst surface, thus diminishing the catalyst efficiency with time and high residual leftover in the process [37,38]. Due to carbon black formation, catalysts are often unrecognizable from the solid residue formed during gasification. This limits their reusability, as well as the increased costs. A cheaper alternative is thus required to make the catalytic conversion of tires possible.

Spent fluid catalytic cracking (FCC) catalyst from the petroleum industry can offer as a good catalyst for waste tire gasification. To increase the output of gasoline and other hydrocarbons produced from crude oil, the petroleum industry uses FCC catalyst as a hydrocracking, hydro refining, and catalytic reforming catalyst [39,40]. The FCC catalyst is replaced when it is degraded and constitutes the largest solid waste stream from the petroleum industry. Due to the presence of heavy metal impurities in FCC it is regarded as hazardous waste. However, the presence of metallic oxides which act as reaction catalysts elsewhere makes the FCC a favorable candidate for use in pyrolysis and gasification [40,41]. Since waste tires are made from petroleum products, the thermal cracking of tires is potentially similar to petroleum cracking and thus FCC catalysts can be used for the catalytic cracking of tar and other hydrocarbons during the gasification of waste tires. Various studies have used FCC catalysts to upgrade tire pyrolysis oil [42–44].

FCC catalysts has also been used for in-situ catalytic waste tire pyrolysis [45–47]. The catalytic effect of FCC catalyst during waste tire pyrolysis has been extensively studied, and it has been demonstrated that adding FCC catalyst to the bed material produces syngas with very low tar content, eliminating the need for an additional tar cracking reactor.

In this work, we explore the catalytic effect of spent FCC catalysts during the CO_2 assisted gasification of waste tires as it can simultaneously provide energy recovery and carbon utilization pathway. The syngas evolved during pyrolysis and CO_2 gasification of waste tires were evaluated and compared to understand the influence of CO_2. The effect of catalyst position on syngas yield during CO_2 gasification was investigated to examine the role of catalyst contact with the solid-phase and the volatiles from waste tires on the catalytic activity. The influence of temperature during catalytic CO_2 gasification of tires was also evaluated to compare catalytic activity vs thermal enhancement on syngas yield and quality.

4.2 Methodology

4.2.1 Materials

Recycled waste tires comprising of the side wall and treads were chopped up to a uniform size of about 2 mm and were used for lab-scale studies on pyrolysis and gasification. The rubber parts were carefully separated out from the fibers such that only the rubber parts were used in the tests. Table 4.1 shows the proximate and ultimate analysis of waste tire used in the lab-scale experiments [48]. The spent fluid cracking catalyst (FCC) was a commercially available catalyst. The catalyst was used as sourced without further preparation. The Energy-dispersive X-ray (EDS) analysis of the catalyst is shown in Figure 4.1. In FCC plants, the catalyst was constantly removed, and new catalyst added, the received FCC catalyst is a combination of used and new FCC catalyst after the oxidation of coke deposits.

Table 4.2. Proximate and ultimate analysis of waste tire [48].

Ultimate Analysis (Dry and Ash free)			Proximate Analysis		
C	81.85	wt.%	Moisture	0.7	wt.%
H	6.66	wt.%	FC	27.9	wt.%
N	1.7	wt.%	VM	62.5	wt.%
O	8.42*	wt.%	ASH	8.9	wt.%
S	1.37	wt.%	LHV	33.33	MJ/kg

**Calculated by subtraction*

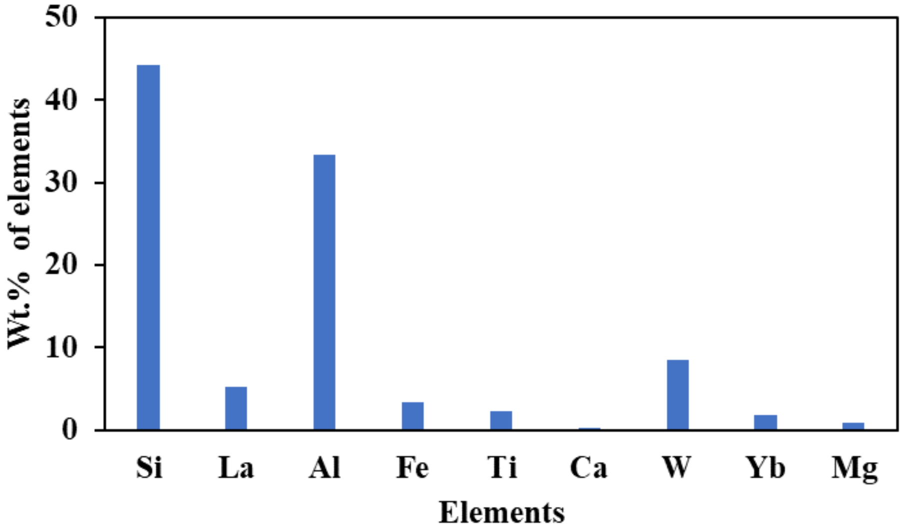

Figure 4.1 Energy-dispersive X-ray (EDS) analysis of spent FCC catalyst.

4.2.2 Experimental method

Catalytic CO_2-assisted gasification and pyrolysis experiments using waste tires were investigated in a semi-batch lab-scale reactor facility. Figure 4.2 shows a schematic diagram of a lab-scale reactor facility. This reactor facility comprises two electrically heated furnaces (a preheater and a gasification reactor), three condensers, a pump, three filters (two 7-micron and one 2-micron filter), five gas sampling bottles, and a micro-GC (Agilent 3000) that provided the molar composition of the tar free and moisture free dry gases. 99.998% pure N_2 and 99.9% pure CO_2 cylinders were used for input gas supply with flow rates controlled using orifice flow meters.

Once the reactors reached desired setpoint temperature and the gasifying agent and tracer gas flow rates are set, the feedstock/catalyst sample held in a wire-mesh sample holder (held together using quartz wool) was introduced into the reactor via a quick disconnect joint. Some of the evolved gases were vented out while the rest of the gases were condensed and filtered using ice baths and sintered filters to produce syngas free from tar, moisture, and particulates. For the first 4 minutes, the syngas samples were collected in the gas bottles for their analysis later, and from 5 minutes onwards, the syngas was analyzed directly online at every 2.66 minutes (GC method time) using micro-GC which was calibrated to analyze H_2, CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8, and N_2 gases with an error in their composition of less than 1%. It employs a molecular sieve and PLOT-U columns connected to thermal conductivity detector.

Using the relative composition of these components with respect to N_2 composition, and the known inlet N_2 flow rates, we calculated the mass flow rate and further cumulative yield of each gas component produced during the pyrolysis and gasification. A detailed description of this facility and the flow rate calculations is given elsewhere [49–51].

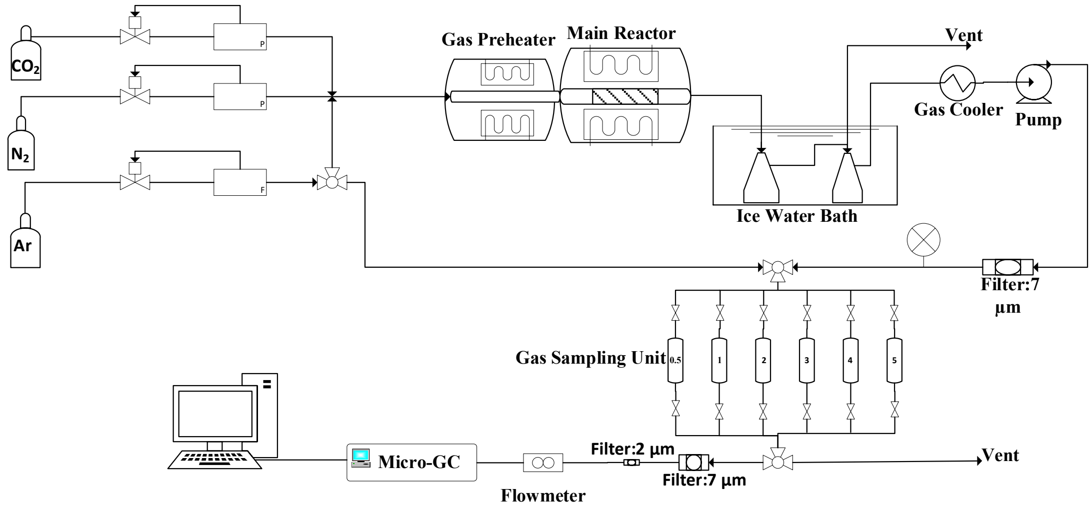

Figure 4.2. Schematic of the experimental setup used for pyrolysis and CO_2-assisted gasification.

For the pyrolysis tests, 2.1 standard liters per minute (slpm) of N_2 was used for the carrier and tracer gas for providing the inert conditions in the reactor and quantification for all the gases evolved. CO_2 at a flow rate of 1.575 slpm (standard liter per minute) was employed as the gasifying agent along with N_2 at a rate of 0.525 slpm as the tracer gas for the gasification studies. The waste tire to catalyst mass ratio for the catalytic tests was chosen to be 5:1. Therefore, for the in-situ catalytic studies, 2 g of catalyst was uniformly mixed in 10 g of the waste tires.

In-situ and quasi-in-situ catalytic approaches were used to understand the effect of catalytic configuration on the syngas evolution and yield during CO_2-assisted gasification. The results were compared with those from no catalyst case. The catalyst in the in-situ configuration was in direct contact with the waste tires, while it was close but not in direct contact with the decomposing feedstock in the quasi-in-situ method. In a fixed bed setup, for quasi-in-situ studies, the catalyst's weight was equally distributed downstream of the waste tire and held in place using quartz wool and stainless-steel wire mesh. The feedstock bed, placed upstream of the catalyst bed, was separated by a distance of approximately 0.3 inch [52]. The reactivity of CO_2-assisted gasification and the influence of catalyst was examined at two different temperatures of 900 ºC and 950 ºC. In all tests, the feedstock amount was kept constant at 10 grams and the catalyst at 2 grams for the in-situ configuration.

4.3 Results and discussion

4.3.1 Comparison of pyrolysis and gasification

Figure 4.3 shows the evolutionary behavior of syngas during catalytic and non-catalytic waste tire pyrolysis and gasification. The characteristics of pyrolysis and CO_2-assisted gasification reactions are compared at 900°C temperature. Figure 4.3(a) shows that for the non-catalytic case, the yield of H_2 is higher for pyrolysis compared to CO_2-assisted gasification. H_2 is likely reformed by CO_2 to H_2O via reverse water gas shift reaction to result in a lower evolution peak during CO_2-gasification. However, for both pyrolysis and gasification, the addition of 16.67 wt.% (2 grams) of FCC catalyst nearly doubled the hydrogen peak. The peak value increased from 0.018 g/min to 0.035 g/min with CO_2-assisted gasification and from 0.025 g/min to 0.042 g/min during the pyrolysis case. It is evident from the results that direct in-situ addition of the FCC catalyst promoted the thermal cracking and dehydrogenation reactions of the larger hydrocarbons leading to increased H_2 yield.

Figure 4.3(b) shows the evolutionary behavior of CO. Since tires contain less than 5 wt.% of O_2 [53], there is no oxygen to react with char/carbon and thus a very small amount of CO was produced during pyrolysis. The addition of FCC catalyst improved the CO yield during pyrolysis by a small margin. The influence of FCC on the evolutionary behavior of CO is clearly seen during CO_2 gasification. During the first 10 minutes the FCC catalyst aids the reforming of hydrocarbons, however after 10 minutes, the CO evolution for both catalytic and non-catalytic cases remains similar. This suggests that after 10 minutes all volatiles have evolved out and the CO production is from the slow CO_2 reaction with char (Boudouard reaction). At this point, the catalyst was found not to influence the char gasification. The catalytic activity was only effective when the tars and other condensable hydrocarbons are formed.

Figures 4.3(c) and 4.3(d) show the effect of FCC catalysts on the production of CH_4 and C_2H_x (C_2H_4, C_2H_2, and C_2H_6). The presence of FCC catalyst increased the CH_4 production since larger hydrocarbons are reformed/cracked into smaller (light) hydrocarbons including methane. Comparing pyrolysis and gasification, CO_2-assisted gasification provided a higher yield of CH_4 compared to pyrolysis. Hence the presence of FCC catalysts aided in the production of CH_4. However, the opposite was observed for C_2H_x. Non-catalytic gasification had the highest but sharper peak compared to catalytic and non-catalytic pyrolysis. While FCC catalyst significantly reduced the peak height of C_2H_x by nearly 50% for the catalytic gasification case, its presence during pyrolysis did not seem to influence C_2 hydrocarbon evolution. This suggests that FCC catalyst's relationship to C_2H_x is via volatiles reforming in the presence of CO_2 which can be heterogeneously enhanced with the presence of the catalyst. Figure 4.4 shows the effect of catalyst addition on the overall yield and energy of syngas (based on lower heating value of syngas components). The most apparent feature from Figs. 4.3& 4.4 is that the addition of FCC catalyst significantly increased the yields of syngas components and that CO_2-asssited gasification produced syngas that was more energetic, indicating that CO_2 intensified the energy recovery of waste tires. Energy yields from catalytic pyrolysis and gasification seem to be similar while their compositions were varied in their CO and hydrocarbon content. This suggests that the significant difference between catalytic pyrolysis and gasification has been the catalytic dry (CO_2) reforming of lower molecular weight hydrocarbons such as C_2 hydrocarbons to form CO.

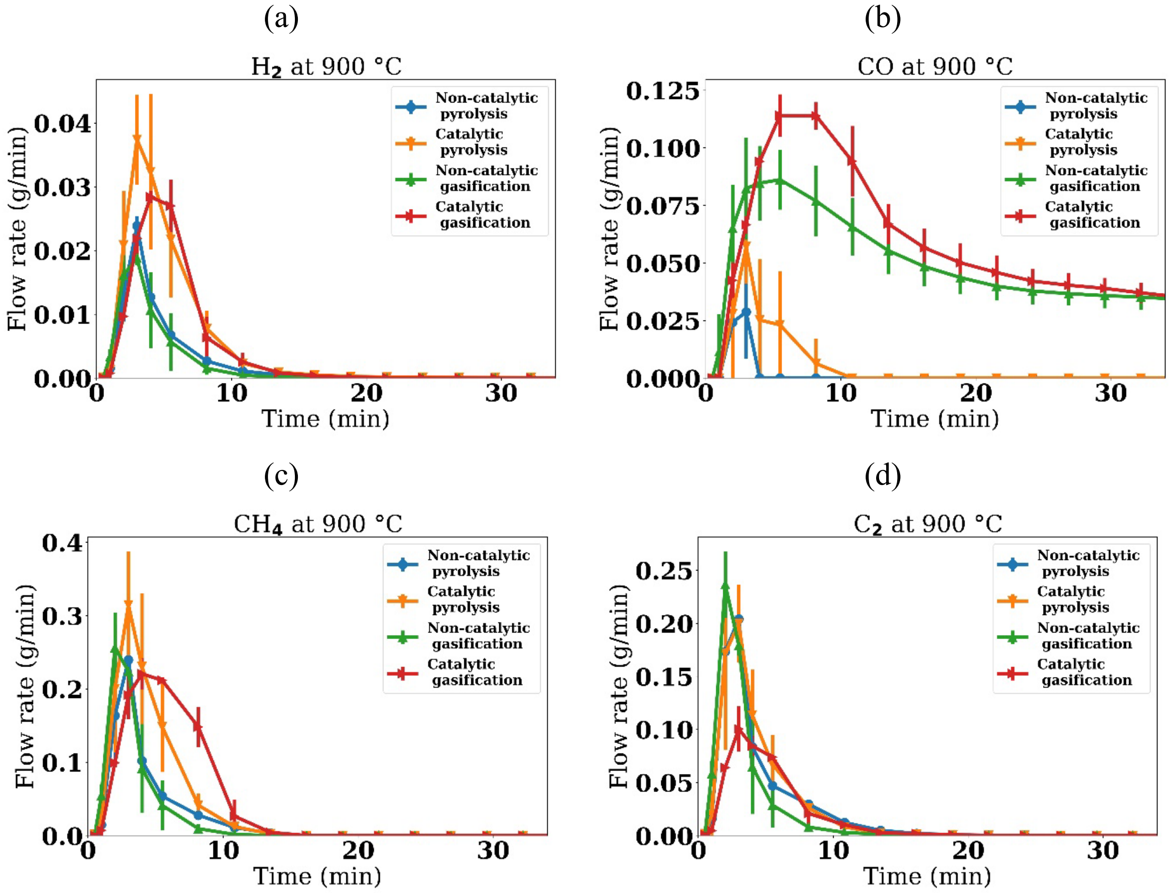

Figure 4.3. Temporal evolution of (a) H_2, (b) CO, (c) CH_4, and (d) C_2H_x flowrates during pyrolysis and gasification of waste tires, both with and without catalyst.

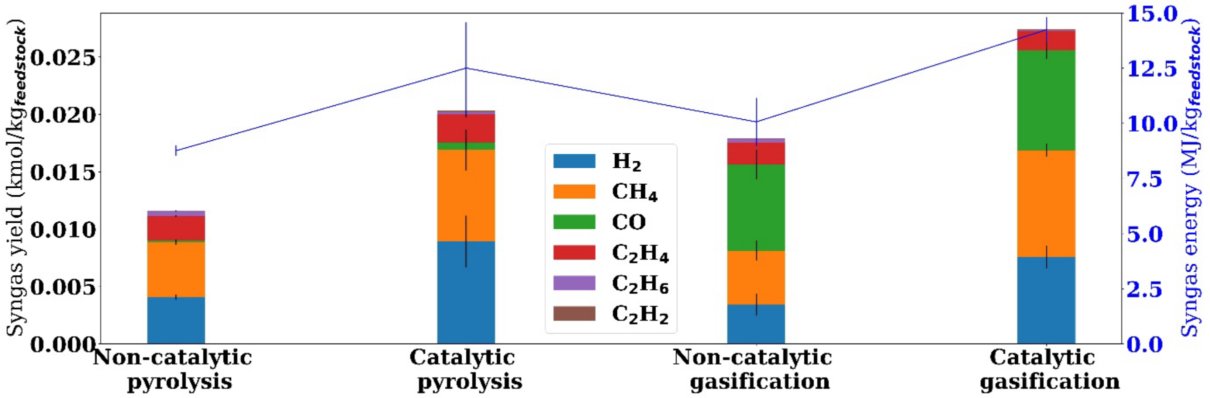

Figure 4.4. Combustible gas yield (bar plot) and energy yield (line plot) from pyrolysis and gasification of waste tires, without and with the fluid catalytic cracking (FCC) catalyst.

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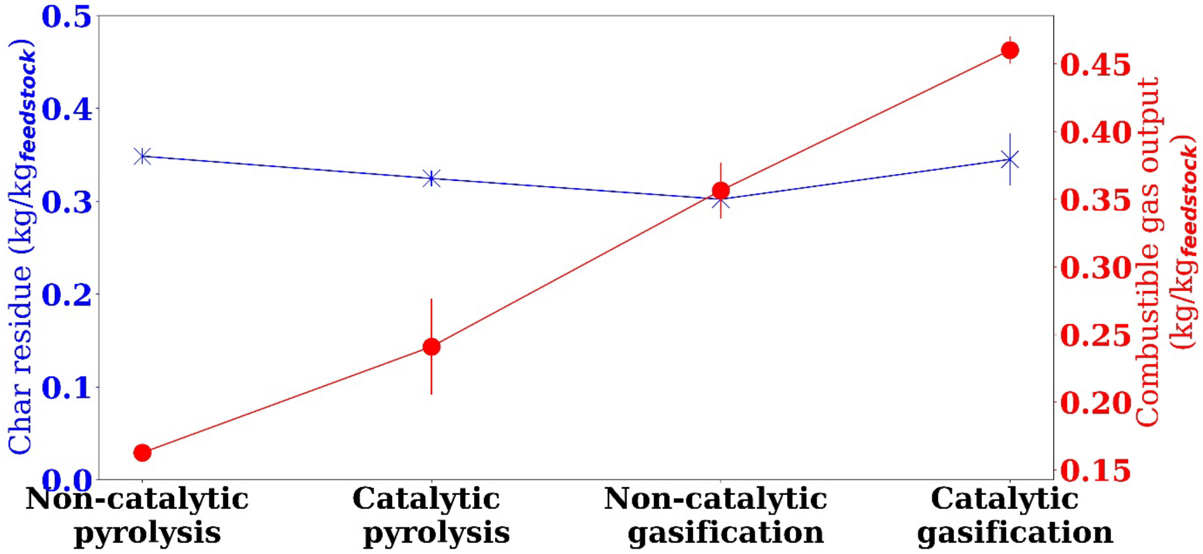

Figure 4.5. Effect of fluid catalytic cracking (FCC) catalyst on pyrolysis and CO_2-assited gasification of waste tires at 900 °C.

Figure 4.5 reveals the influence of FCC catalyst on the mass-based conversion of waste tires into char and gas yields from pyrolysis and CO_2-asssited gasification. Here, combustible gas yield includes the aggregate of H_2, CO, CH_4 and C_2H_x (with x=2, 4 or 6) yields while the char yields include the solid residue that excludes the catalyst mass. Thus, the char yields in Fig. 4.5 include both the char and coke deposit yields. Irrespective of the presence of catalyst, or gasifying agent, the char yields changed minimally by 2-3% to stay above 30 wt.%. But the combustible gas yield increased in the presence of both catalyst and CO_2 addition. So, at 900

°C, although we know from Figs. 4.3& 4.4 that addition of FCC catalyst does not improve Boudouard reaction, we can also see that the contribution of Boudouard reaction to char conversion is minimal. This is contrary to the assumption in Fig. 4.3(b) that after 10 minutes, the CO evolution is from Boudouard reaction. It means, in this Fig. 4.3(b), majority of CO evolution shown was from reforming of volatiles/tar by-products by CO_2. While the CO yield may still seem significant after 15 minutes in Fig. 4.2(b), the CO yield from there to 30 minutes will only account to 0.2-0.3 g of char's carbon conversion and thus the variation in char yields were very low in Figure 4.5. It points to a significantly high thermal stability of tire-char due to the presence of carbon black added for strengthening tires. So, while FCC catalyst can be added, and thermochemical techniques can be improved. This high stability of tire char means, alternative pathways such as reusing as carbon black or aggregate applications are still needed to handle the char without going to higher temperatures or more severe operating conditions that can lower the efficiency and increase costs.

4.3.2 Influence of catalyst position

Spent FCC catalyst is a hydrocarbon cracking catalyst and does not participate in the solid reaction or the solid thermal decomposition of waste tires. It only participates during the thermal cracking of the volatiles that are evolved from the reactor. Figure 4.3 showed that the catalytic activity ends at 10 minutes when all the volatiles are released. Therefore, mixing the catalyst directly with the waste tire may reduce its activity. When mixed directly (herein called in-situ), char /soot formed during waste tire decomposition will build up on the catalyst surface and reduce its activity. By placing the catalyst downstream of the main solid feedstock, its decomposition may improve the thermal cracking of released volatiles.

Wang et al. [52], investigated the influence of catalyst (Ni/Al_2O_3) position during the CO_2-assisted gasification of polypropylene. Their results revealed better catalytic activity with catalyst placed downstream of the feedstock (herein called quasi-in-situ configuration) in the thermal decomposition of polypropylene into H_2 and C_mH_n than the in-situ catalytic configuration. In quasi-in-situ arrangement, the catalyst is placed downstream and separate from the solid/melt sample in the same reactor. The catalyst forms a fixed bed from which the evolved volatiles must pass through. Catalytic cracking of the hydrocarbons formed from the solid feedstock, using the quasi-in situ arrangement as proposed in [52] is examined here. The results obtained from quasi in-situ case are compared to the in-situ and non-catalytic cases. Figure 4.6(a) shows that in-situ and quasi-in-situ catalytic gasification significantly increased the H_2 yield as compared to non-catalytic gasification. Both in-situ catalytic and quasi-in-situ catalytic gasification cases showed the lasting of H_2 evolution to much later times of 20 minutes than the non-catalytic case, which terminated at about 10 minutes. The results show that in-situ and quasi-in-situ catalytic approaches had higher H_2 peak values and produced more H_2 by between 84.2% and 115.7% in comparison to non-catalytic case. And as observed by Wang et al. [52], greater H_2 yields can be produced with quasi-in-situ than with in-situ catalysis.

Figure 4.6(b) shows a defined improvement in CO production during quasi-in-situ catalytic case compared to in-situ and non-catalytic gasification cases. The peak height of CO increased by 25% and 40% for the in-situ and quasi-in situ methods, respectively compared to the non-catalytic case. After 10 minutes, the CO evolution yields from the in-situ catalytic and non-catalytic cases are equal or comparable, whereas the quasi-in situ yield provided significantly larger yields that continued for the same amount of time. This indicates that the CO enhancement after 10 minutes for the quasi-in-situ process is from the reforming of hydrocarbon that escaped from the primary reaction and condensed on the catalyst surface. However, in both cases, coke formation did not hinder the production of syngas.

Figure 4.6(c) and 4.6(d) show the effect of positioning of the catalyst on the evolution of CH_4 and C_2H_x, respectively. When compared to non-catalytic approaches, both in-situ and quasi-in-situ catalytic methods yielded higher CH_4 yields. The evolution of CH_4 terminated after about 10 minutes for the non-catalytic case while it continued for almost 20 minutes for the in-situ and quasi-in-situ catalytic methods. The quasi-in-situ catalytic gasification provided a higher peak height for CH_4 by 55% compared to in-situ and non-catalytic methods. The results reveal that the FCC catalyst improves the yield of CH_4 as the smallest hydrocarbon. C_2H_x evolution peak from quasi-in-situ case was close to non-catalytic case but with prolonged evolution whereas in-situ catalysis led to lowered peaks and evolution rate compared to non-catalytic case. This means the presence of FCC catalyst further thermally cracked higher (larger) hydrocarbons to provide C_1 and C_2 hydrocarbons, but in-situ mixing limits this cracking to have only H_2 and CH_4 enhancement while C_2 hydrocarbons decrease.

Comparing Fig. 4.6(d) and Fig. 4.3(d), one can see that FCC catalyst did not influence C_2H_x evolution from pyrolysis and in non-catalytic gasification, CO_2 addition also only minimally influenced its evolution. But FCC catalyst increased C_2H_x evolution (albeit delayed) via quasi-in-situ mode but only after 5 minutes, while mixing it decreased its evolution. This means, FCC catalyst addition improves CO_2 reforming of volatiles along with cracking reactions but their effective influence on the evolution of C_2H_x are a resultant of consumption reaction via reforming and production reactions via cracking.

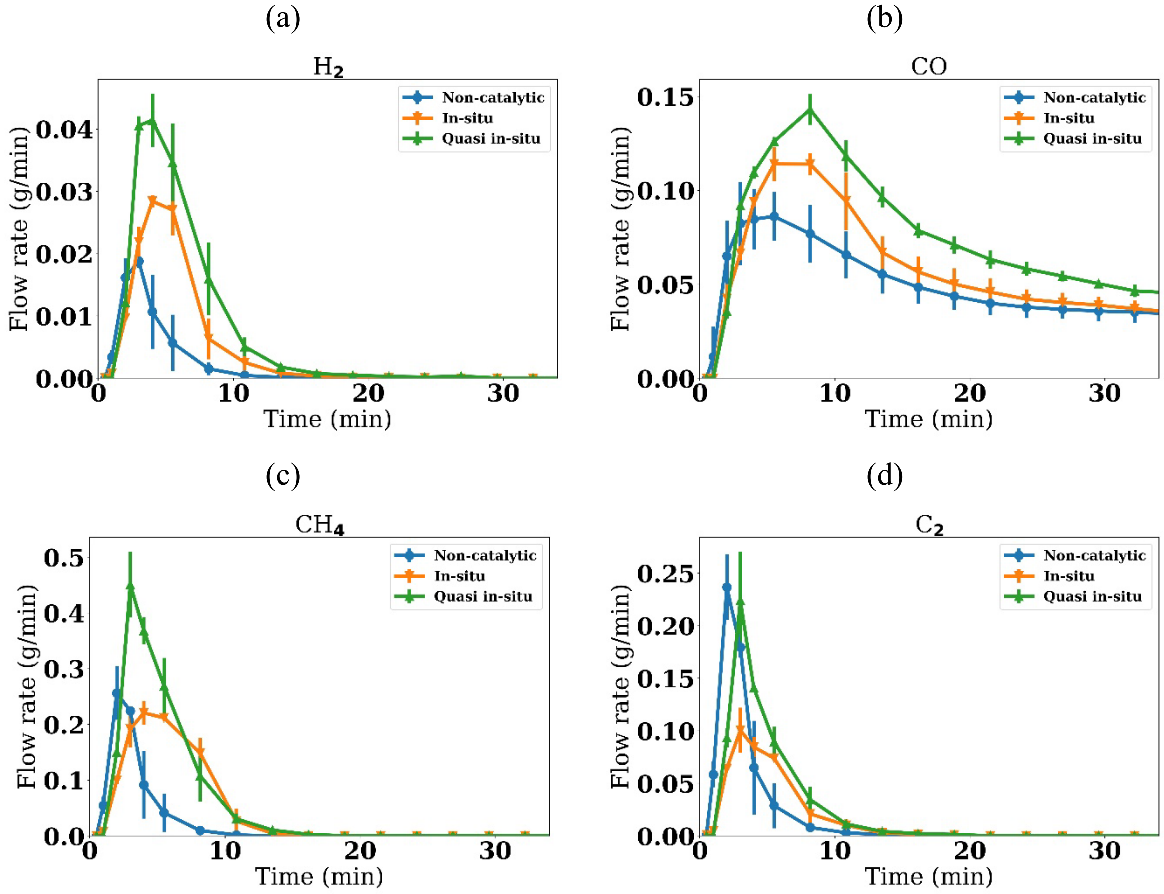
(a) (b) (c) (d)

Figure 4.6. Temporal evolution of (a) H_2, (b) CO, (c) CH_4, and (d) C_2H_x flowrates during in-situ, quasi-in-situ and non-catalytic gasification of waste tires.

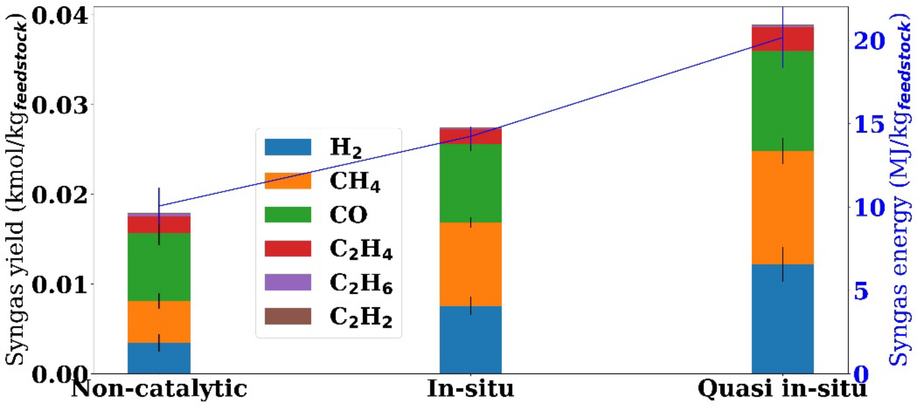

Figure 4.7. Combustible gas yield (bar plot) and energy yield (line plot) during in-situ, quasi-in-situ, and non-catalytic CO_2-assisted gasification of waste tires.

The results on the total syngas component yield and syngas energy from the in-situ, quasi-in-situ, and non-catalytic gasification of waste tires are shown in Figure 4.7. When compared to non-catalytic case, the in-situ and quasi-in-situ catalytic cases provided greater overall syngas yields. The in-situ and quasi-in-situ catalytic cases increased the syngas energy production by around 50% and 100%, respectively (see Fig. 4.7). High syngas molar and energy recoveries were achieved via quasi in-situ mode suggesting the effectiveness of separating the catalyst to avoid inhibitions in close contact with the feedstock. 20 MJ of energy (based on lower heating value of syngas components) was recovered in the form of syngas in quasi-in-situ gasification which is approximately above 65% of the net calorific value of waste tires. This proves the effectiveness of FCC incorporation to enhance energy recovery from waste tires via quasi in-situ mode of gasification.

Catalyst configuration is found to be important for the thermal cracking of hydrocarbons, see Wang et al. [52]. The FCC catalyst did not participate in the solid-solid reaction and the gas-solid (feedstock/char) reaction, but instead, participated in the degradation of hydrocarbons that occurs in the gas phase and the reforming reactions. Since waste tires were much larger than the catalyst in this case, a homogeneous mixture could not be created for the direct in-situ case to have adequate time for their contact and to catalyze the vapor phase reactions. In addition, since the CO_2-char reactions are slow enough to remove the char, the development of char or soot on the catalyst's surface lowers the catalytic activity for the in-situ case. As a result, the downstream quasi-in-site was more effective and efficient. In the quasi-in-situ catalytic case, the tar produced from the breakdown of waste tires reacted right away with CO_2 to transform it into gases as it flowed through the catalyst bed, which was kept at the same temperature. The tar vapors here offered a better contact with the catalyst than they did in the in-situ case, thus increasing the likelihood of enhanced H_2, CO, and CH_4 production in the quasi-in-situ case.

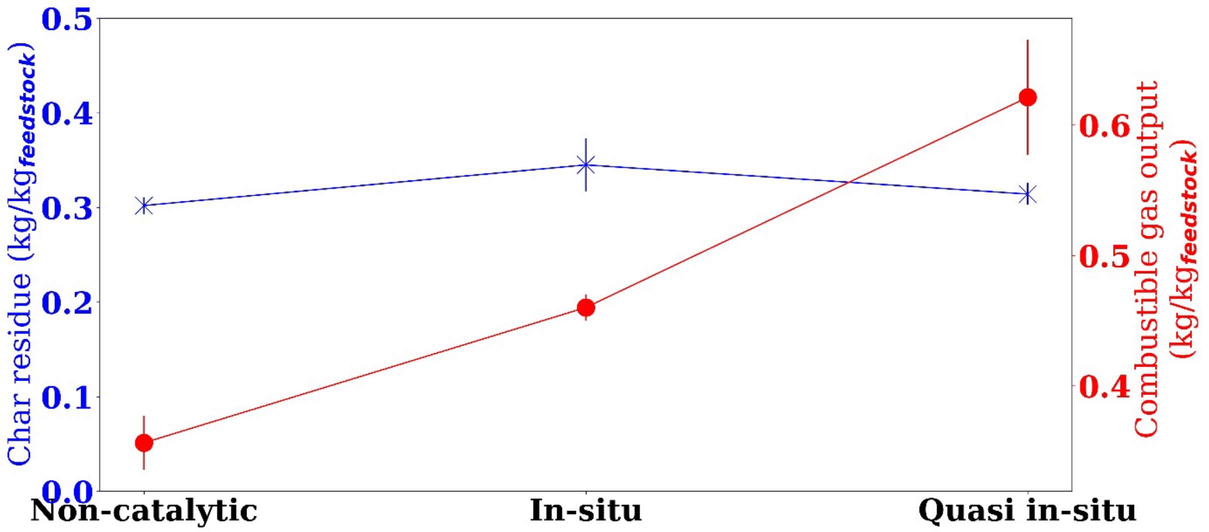

Figure 4.8. Effect of FCC catalyst position on CO_2-gasification of waste tires at 900 ºC.

Figure 4.8 shows the effect of FCC catalyst incorporation and its position on the char and combustible gas-yields from waste tire gasification on mass-basis. Combustibles increased by as much as 100% in quasi in-situ catalysis compared to non-catalytic gasification while in-situ catalysis only increased it by around 30%. The changes in char yield were minimal as before, hovering between 30-35 wt.% as any enhancement of syngas recovery from FCC catalyst only contributes to very small carbon loss from the forming char.

4.3.3 Effect of temperature

Boudouard reaction, CO_2-reforming, and the thermal cracking of hydrocarbons are all endothermic reactions that are highly affected by temperature in CO_2-assisted gasification. Thermodynamic calculations showed that the Boudouard reaction is spontaneous only above 700 ºC to favor CO production [54]. An increase in temperature further promoted CO production. Another study [55] showed the C-CO_2 reaction is slow due to the mass transfer limitation caused by the intraparticle diffusion of CO_2. Pore size influences the diffusion rate of CO_2. At higher temperatures, the pore size of the char increases allowing more CO_2 to diffuse thus improving CO_2 gasification. Sadhwani [55] showed that in CO_2-assisted gasification of biomass, an increase in temperature from 850 ºC to 934 ºC increased the surface area of char micropores from 237.7 m^2/g to 350.5 m^2/g and also the total pore volume from 0.06202 cc/g to 0.1428 cc/g. Our present results show the same evolutionary behavior, see Fig 4.9. An increase in temperature from 900 ºC to 950 ºC increased the yield of syngas (H_2, CO, and CH_4) and reduced the yield of higher series of hydrocarbons, larger than methane. H_2 evolution peak increased by nearly 226% for the non-catalytic and by 85.7% for the in-situ catalytic case as the temperature was increased from 900 to 950 °C.

Figure 4.9 shows much higher syngas yield for the non-catalytic higher-temperature gasification case than the in-situ catalytic high-temperature gasification case. At high temperatures, the hydrocarbons are cracked faster, that and promotes CO_2 diffusion into the char thus allowing for the reforming reactions of volatile that lie on the surface of the char. The presence of in-situ catalyst inhabited reactions due to the heat transfer limitation as well as soot formation that builds on the catalyst. This can be seen from the deviation between catalytic and non-catalytic gas evolutions only after 5 minutes for gasification at 950 °C.

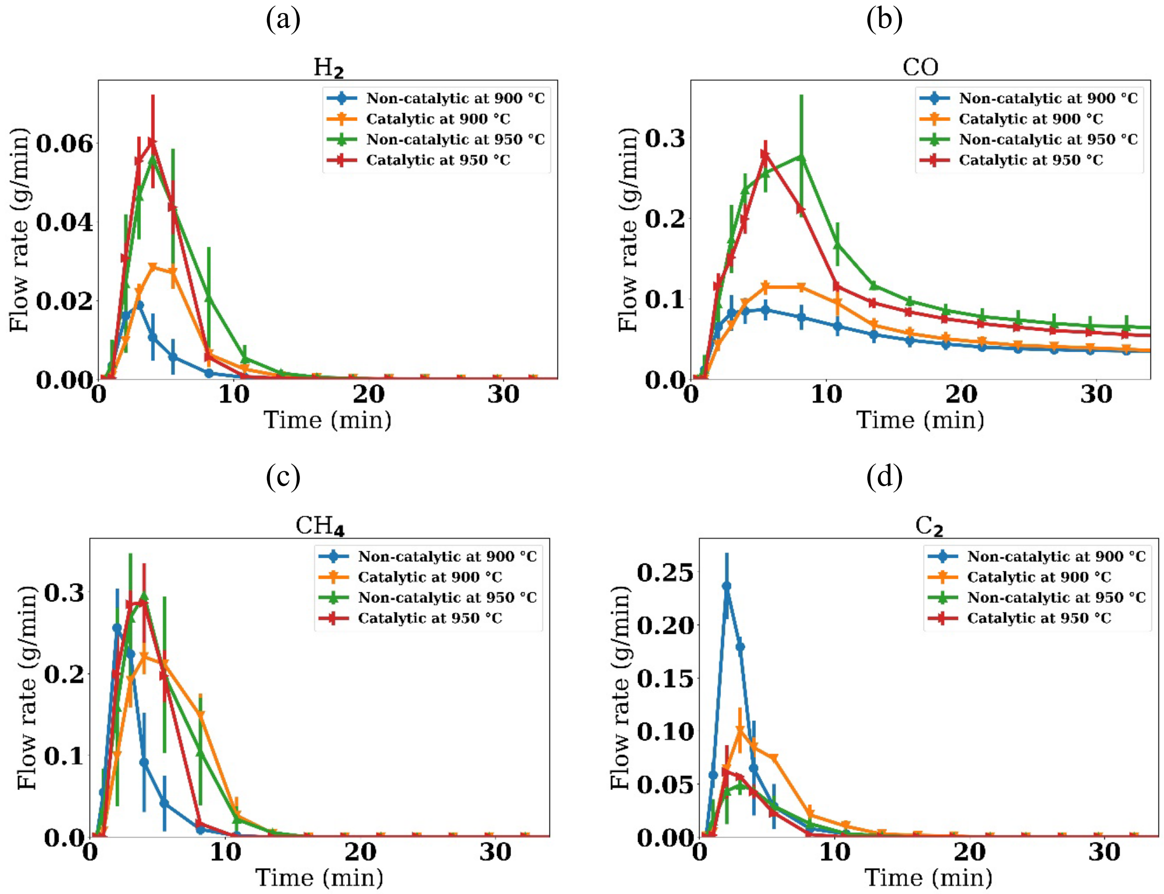

Figure 4.9. A comparison of temporal evolution of (a) H_2, (b) CO, (c) CH_4, and (d) C_2H_x flowrates during catalytic and non-catalytic gasification of waste tires at 900 °C and 950 °C.

Figure 4.10 shows a comparison of the cumulative syngas components' molar and energy yields from the noncatalytic and catalytic gasification of waste tires at 900 °C and 950 °C.

Increase in temperature from 900 to 950 °C provided a greater increase in the overall syngas yields by 143.75% for the catalytic case and by 187.5% than the non-catalytic case, and as compared to the non-catalytic 900 °C gasification case. The non-catalytic 950 °C and catalytic 950 °C cases provided increased syngas energy production by 110.5% and 78.9%, respectively, see Fig. 4.10. Non-catalytic case at 900°C provided overall syngas energy yield of only 9.5 MJ/kg, while it increased to around 15 MJ/$kg_{feedstock}$ for catalytic case at 950 °C, and 17 MJ/$kg_{feedstock}$ for non-catalytic case at 950 °C.

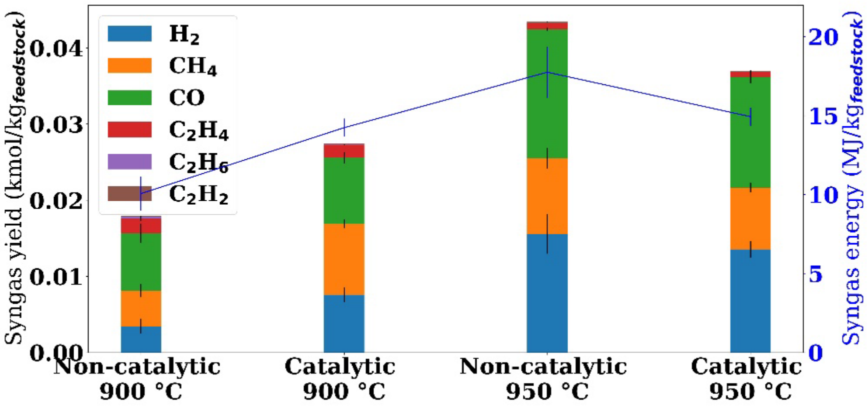

Figure 4.10. Combustible gas yield (bar plot) and energy yield (line plot) from CO_2-assisted gasification of waste tire at 900 and 950 °C with and without FCC catalyst.

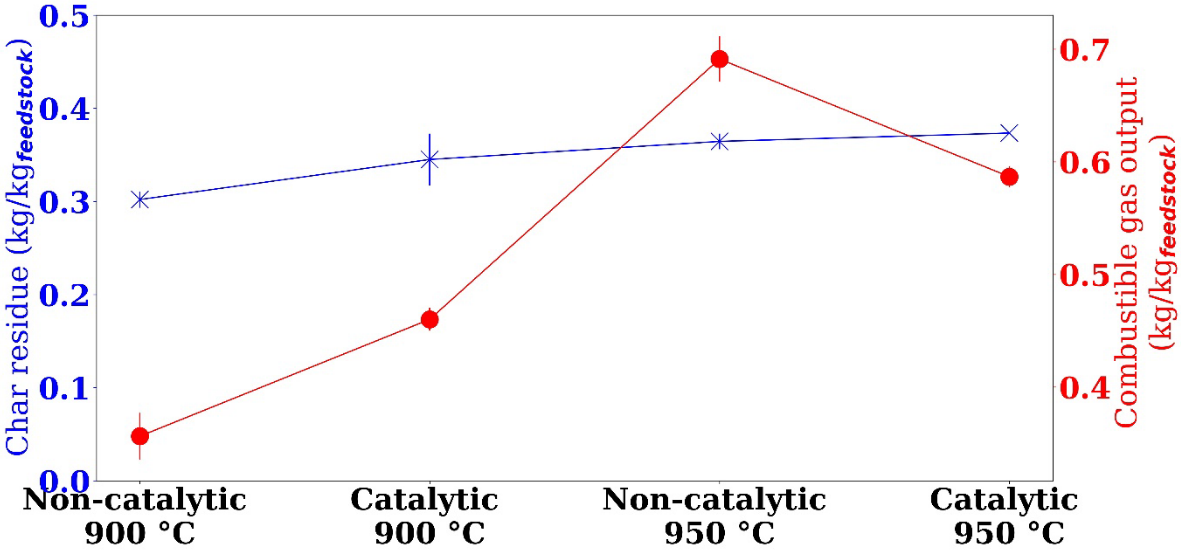

Figure 4.11. Effect of FCC catalyst on pyrolysis and CO_2-gasification of waste tires at 900 and 950 °C temperatures.

Figure 4.11 reveals the effect of temperature on char and gas yields from in-situ catalytic and non-catalytic gasification. The char yield results are a significant revelation showing that increase in temperature did not have any influence on the char conversion irrespective of catalyst. This suggests a significantly high reaction inertness of the tire-char and as described above, alternative utility or conversion pathways are needed for their handling. Increase in temperature increased combustible gas yields significantly, but at 950 °C non-catalytic mode provided better conversion than in-situ catalytic gasification. This suggests that as the temperature is increased, the inhibitive behavior of FCC catalyst when mixed directly is more prevalent as the kinetics and equilibrium of these reactions are driven forward significantly at these temperatures and reactions such as CO_2-reforming are blocked by the catalyst. Comparing Figs. 4.10 and 4.11 with 4.7 and 4.8, one can see that to improve syngas and energy recovery from waste tires, while FCC catalyst incorporation is viable, its presence in quasi-in-situ mode is more favorable compared to simply increasing the temperature.

4.4 Conclusions

In this paper, we have examined the influence of spent FCC catalyst on the pyrolysis and gasification of waste tires to better understand the capabilities and potential of FCC catalysts in assisting the thermal cracking of waste tires into syngas. The impact of catalyst position (in-situ and quasi-in-situ catalytic modes) on syngas yield in CO_2-assisted gasification was examined at 900 °C and 950 °C. The results showed that both catalytic pyrolysis and gasification produced higher yields of total syngas and syngas energy compared to the non-catalytic cases. However, CO_2-assisted catalytic gasification showed much more improved performance as compared to pyrolysis. Catalytic CO_2-asssited gasification (in-situ) increased the overall syngas yield by 81.25% compared to non-catalytic gasification, by 205.5% compared to non-catalytic pyrolysis and by 44.7% compared to in-situ catalytic pyrolysis, respectively. Catalytic CO_2 gasification also increased the syngas energy by 160%, 78.9%, and 19%, compared to non-catalytic pyrolysis, non-catalytic gasification, and catalytic pyrolysis cases, respectively. In terms of catalyst position the quasi-in-situ catalytic gasification provided higher syngas yields and syngas energy compared to the in-situ catalytic gasification using the same FCC catalyst. A comparison of quasi-in-situ gasification to in-situ catalytic gasification showed syngas and energy yields increased by 24% and 23%, respectively, which implies that quasi-in-situ catalytic gasification is more efficient and effective at increasing the syngas yield and provided energy recovery as high as 20 $MJ/kg_{feedstock}$. Increase in temperature also improved the syngas yield and energy. However, the catalyst activity decreases at high temperatures for the in-situ case due to soot/coke formation on the catalyst surface at high temperatures and blocks the diffusion of CO_2 with volatiles for reforming. The results reported here clearly demonstrate the synergistic capabilities for integrating waste materials from FCC plants and tire recovery facilities to recover valuable products and reduce the carbon footprint via catalytic CO_2-assisted gasification.

Acknowledgments

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5 Co-gasification of waste tires and gypsum

Manuscript

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Short summary

In this work we conduct an experimental test on a fixed bed reactor with two furnaces, to investigate the effects of gypsum mass proportions on syngas evolution when waste tires are gasified with gypsum in CO_2 atmosphere. Tires contained less than 5% by mass of oxygen, this means for every mole of tire the ratio of carbon to oxygen is 50:1 whereas that of carbon to hydrogen is 1:1. If the designed syngas must have a ratio H_2/CO above one, it, therefore, means a significant amount of carbon will remain uncovered unless an external amount of oxygen is added in proportions to the carbon in the tire. As a result, during gasification, waste tires produce significant amounts of tar, and unreactive char is formed. Therefore, an external amount of oxygen is required to produce the CO in the syngas. This source of oxygen is important since oxygen addition in thermochemical processes leads to CO_2 emissions. Gypsum is a waste stream from the construction and demolition sector, which when in an anhydrite state ($CaSO_4$) contains 4 moles of oxygen for every mole of gypsum. This makes gypsum an excellent oxygen carrier. It is thus postulated that the addition of gypsum will increase the evolution of syngas since gypsum will react with uncovered char and tar through the solid-solid reaction or $CaSO_4 + 4\ C = 4\ CO + CaS$ to produce CO. The use of CO_2 improves the yield of syngas. CO_2 will react with the volatiles through a reforming reaction while gypsum reacts with the char and higher hydrocarbons such as tar. Indeed, it was shown that gypsum addition to the waste tire feedstock provided increased syngas production and quality through increased low heating value (LHV) of the syngas.

Declaration by canditate:

The scope of my contribution to the chapter is as follows:

Planning Experiments	70%
Conducting the experiments	90%
Results interpretation	80%
Compilation fo chapter	100%

The following co-authors have contributed to this chapter as per following:

Co-author	Nature of contribution		Contact and signature
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I declare that the above information is true and reflects the nature and extent of the contributions of the candidate and the co-authors

Signature of candidate:……………………..

Date:…………………….

Syngas Production from Co-gasification of Waste Tires and Gypsum

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Abstract

Syngas production from co-gasification of waste tire and different amounts of drywall waste (gypsum, ($CaSO_4$)) was investigated using CO_2 as the gasifying agent in a lab-scale reactor. Gypsum is known to react with carbon feedstocks through solid-solid reactions to produce CaS and CaO, CO, and CO_2. The presence of gypsum in waste tires increased the syngas yield from the conversion of char and tars. Gypsum addition to the waste tire also increased syngas quality from increased syngas energy yield. The overall yield of syngas increased by up to 55% while the energy yield (MJ/ kg feedstock) improved by 40% with gypsum addition. The product gas yield, energy, H_2 and CH_4 yields increased with gypsum addition while CO only increased for lower gypsum concentrations. CO_2 yields increased for higher gypsum addition instead of CO. Aspen Plus simulation results revealed that for waste tires, temperatures < 1200 ºC suppressed the transformation of sulfur present in gypsum into SO_2 for all waste tires to gypsum feed mass ratios. At 50 wt.% gypsum concentrations, only 2% of the sulfur in the feedstock was transferred into SO_2. The results showed improved syngas yield and quality, without any increase in sulfur emissions showing the benefits of gypsum waste incorporation in waste tire gasification.

5.1 Introduction

Urbanization and industrialization have led to a rapid increase in the number of road vehicles, which generates massive amounts of waste tires. The USA alone generated over 274 million scrap tires representing over 5 million tons of scrap waste tires in 2021 [1]. Europe produced

4.24 million tons of tires in 2020 [2]. The amount of waste tires has also increased in developing countries. For example, in 2022 South Africa generated an estimated 250,000 metric ton of waste tires adding to an existing stockpile of 900,000 metric ton spread across 26 national storage depots without a robust plan for reprocessing or recycling [3,4]. Some of these waste tires end up illegally disposed in open fields which leads to breeding sites for mosquitoes and rodents and also gives rise to accidental fires with high levels of pollutants emission that causes health hazards [5]. Wastes tires present a major environmental issue as they are not biodegradable due to the high stability of the polymers, as well as the presence of metals and other inorganic chemicals. While most of the developed world has been successful in managing tire waste through recycling and reuse initiatives, developing countries still trail behind in establishing a successful end-life tire management strategy [6]. As an example, in South Africa, the recycling and reuse of waste tires are about 20% while the rest are stockpiled [3]. Whereas in Europe the recycling and reuse rate is more than 95% [7]. The European Tire and Rubber Manufacturers' Association (ETRMA) reports that by 2019, about 95% of waste tires were collected and treated for material recycling and energy recovery [8]. In the United States (US), over 95% of stockpiled tires have been cleaned up by 2021 and the recycling and reuse rate is more than 71% [1]. Even then, a significant portion of waste tires will be generated every year, therefore alternative technologies with higher processing capacity and minimal carbon emissions must be installed to deal with this rising waste.

Waste tires represent a petroleum waste stream with a high carbon component and have a comparatively high caloric value, making them competitive with other types of fuel, such as coal, and biomass which have much lower calorific value [9]. Fossil fuels remain the major source of South Africa's energy needs with only 2% coming from alternate sources [10]. Successful conversion of waste tires to power would improve the country's energy mix and alleviate some of the dependency on expensive fossil fuels such as diesel. Alternatively, waste tires can be used to produce a vast array of chemical products through thermochemical conversion processes such as gasification, pyrolysis, liquefaction, and devulcanization. Thermochemical conversion, which uses gasification and pyrolysis to produce syngas, liquid fuels, char, and high-quality byproducts including carbon black and nanomaterial, is a promising waste tire disposal method [11].

This work examines the synergy of co-gasification of waste tires with gypsum waste from the construction and demolition industry. Process value can be improved when the two-waste materials are co-processed. Synergetic interaction between waste tires and gypsum is expected to improve the conversion of waste tires to syngas and convert the gypsum to valuable chemicals such as quicklime and calcium sulfide. During gasification, waste tires produce significant amounts of tar and unreactive char. The char from waste tires is relatively more stable compared to other types of feedstocks, making this a substantial challenge in terms of conversion efficiency. Recent studies have shown that when different feedstocks are co-gasified, improved product quality, energy efficiency, and poly-generation of products for market flexibility are realized [12]. Policella et al [13] showed that quality syngas can be achieved with CO_2-assisted gasification which mitigates two environmental pollutants (CO_2 and waste tires). Co-pyrolysis of waste tires and maize stalk increased the yield and quality of syngas [14]. The use of CO_2 recycled as a gasifying agent increase the yield of hydrogen resulting in an increase of energetic and exergetic efficiencies by 59.58 and 49.39%, respectively[15]. Synergetic interaction was observed in the co-pyrolysis of waste tires with low-rank coal [16], pine bark[17], rice straw [18] and corn stover [19]. Lahijani et al [20] showed that CO_2 assisted gasification is effective on char reactivity when tires are blended with biomass. Czerski et al [21] used different biomass ashes as catalysts to promote tire char reactivity during CO_2 gasification. Jansen et al [22] investigated the influence Boudouard reaction during waste-tire pyrolysis and gasification of scrap tire rubber crumbs under nitrogen and treatment with pure carbon dioxide. The conclusion drawn from this study is that CO_2-C = CO is active between from 750 ◦C to 1100 ◦C. Studies by other investigators [23–28] have shown that CO_2-gasification of various carbonaceous feedstocks provides excellent opportunities to utilize waste materials and produce energy and quality products.

In this study, the co-gasification of waste tires and gypsum in the CO_2 atmosphere is explored. Gypsum reacts with carbon through solid-solid reactions at temperatures above 700 ºC and produces compounds such as CO, CaS, CaO, and SO_2 depending on process temperature and feed composition [29,30]. $CaSO_4$ will typically decompose at temperatures above 1200 ºC. In the presents of carbon, $CaSO_4$ decomposes at a much lower temperature, which improves the recovery potential of this waste material. Jia et al. [30] studied the mechanistic decomposition behavior of $CaSO_4$ when pyrolyzed with coal. Their results showed that at 800 ºC, $CaSO_4$ (gypsum) was converted to CaS showing that the carbon present in coal was predominantly responsible for $CaSO_4$ decomposition. Co-gasification waste tire char and municipal solid waste with gypsum have also been examined [31,32]. Their results have shown that the presence of gypsum increased the yield of syngas and reduced the char yield. Processing conditions such as temperature were utilized to target specific products. Yang et al. [33] investigated the $CaSO_4$ activity in the chemical looping gasification system, only H_2S was detected in the gaseous sulfide that occurred during its transformation. Solid calcium sulfide (CaS) and a small amount of unreacted $CaSO_4$ were detected at 900 ºC. These results reveal that at moderate temperatures (< 1000 ºC), the risk of producing sulfur dioxide due to the presence of gypsum was minimal. Furthermore, literature reveals that adding gypsum to biomass and MSW combustion can improve ash behavior and avoid agglomeration and defluidization [34,35].

The objective of this work is to experimentally investigate the effect of adding different amounts of gypsum to waste tire in CO_2-assisted gasification on H_2 and syngas production. We also used Aspen Plus® software to investigate the fate of sulfur present in the solid gypsum during its transformation into other products.

5.2 Methodology

5.2.1 Materials

The materials used in this work were all obtained locally. Commercial drywall board was obtained from a local hardware store and peeled to remove the cardboard layering and gather gypsum waste. This was ground to 400-700 microns for all the tests reported here. Recycled waste tires comprising of the side wall and treads were chopped up into chunks of a uniform size of 2 mm. For waste tire-gypsum mixtures, the mass of waste tire was kept constant at 10 g, while gypsum was varied from 2 g to 10 g to provide understand the effect of varying gypsum concentrations in the feedstock. Thus, the gypsum concentration effectively varied from 0-50 wt.% in the waste tire-gypsum mixtures prepared. Table 5.1 provides a summary of the experimental test matrix investigated here. For gasifying agent, pure gas cylinders containing 99.998% nitrogen and 99.9% CO_2 were used.

Table 5.1. Experimental matrix of the operating conditions

	Gypsum mass (g)	**Waste tires mass (g)**	**Temperature (ºC)**	**Gasifying agent**
Case 1	0	10	900	2.1 slpm of 75 vol.% CO_2+25 vol.% N_2
Case 2	2			
Case 3	5			

Case 4	10			

5.2.2 Equipment

The CO_2-assisted co-gasification of waste tires and gypsum was investigated in a semi-batch lab-scale reactor. In this reactor set-up, two electrically heated horizontal furnaces were used to preheat the gasifying agents and heat the feedstock respectively. With gasifying agent flowing and the furnaces were set to the setpoint temperature of 900 °C. Once this is achieved, the feedstock sample (held in a quartz/wire-mesh sample holder) was placed into the furnace through a quick-disconnect coupling at the end of the furnace. This was followed by venting some of the evolving syngas products and condensing a portion of the obtained syngas via three ice bath filters to remove volatile products. This moisture and tar-free syngas was pumped using a peristaltic pump via sintered metal filters for their analysis. While the flow rates of gasifying agents were controlled using orifice flow meters, GC/TCD (Agilent 3000A) was utilized to analyze the dry, tar and particulate free syngas. The GC/TCD was calibrated using refinery gas standard for H_2, O_2, N_2, CH_4, CO, CO_2, C_2H_4, C_2H_6 and C_2H_2. For the first 5 minutes of the reaction, gas sampling bottles were used to acquire and analyze the syngas and from 5 minutes onwards, the syngas was directly analyzed at the GC speed with a sample collected every 2.66 minutes. With known N_2 flow rate going into the reactor and assuming N_2 as inert and not produced in these reactions, the syngas components' molar compositions measured by the GC were compared with respect to the measured N_2 mole fractions to obtain the instantaneous flow rates of the syngas components. Further details of such calculations can be found elsewhere [26,36]. The temperature is chosen to be 900 °C to keep Boudouard reaction active. Each experiment was repeated three times to ensure repeatability.

5.3 Results and discussion

5.3.1 Effect of gypsum on the evolution of syngas components

Figure 5.1(a) shows the effect of increasing gypsum mass proportions in the gasifying sample on the temporal evolution of H_2 during CO_2-assisted gasification of waste tires. The figure shows that for all cases, the evolution of H_2 was complete in the first 20 minutes. The presence of gypsum enhanced the flow rate of H_2. Figure 5.1(a) shows that the evolved H_2 peak increased and widened with the addition of gypsum. The highest peak height of H_2 evolution was achieved using 16.67 wt.% gypsum in waste tire (10gm WT: 2gm gypsum). However, with an increase in gypsum proportion, the peak height decreased, and the peak width increased. 50 wt.% (10gm WT:10gm gypsum) had a much wider evolutionary behavior, which suggests that gypsum interacted with the waste tire through the solid-solid reaction to release more hydrogen.

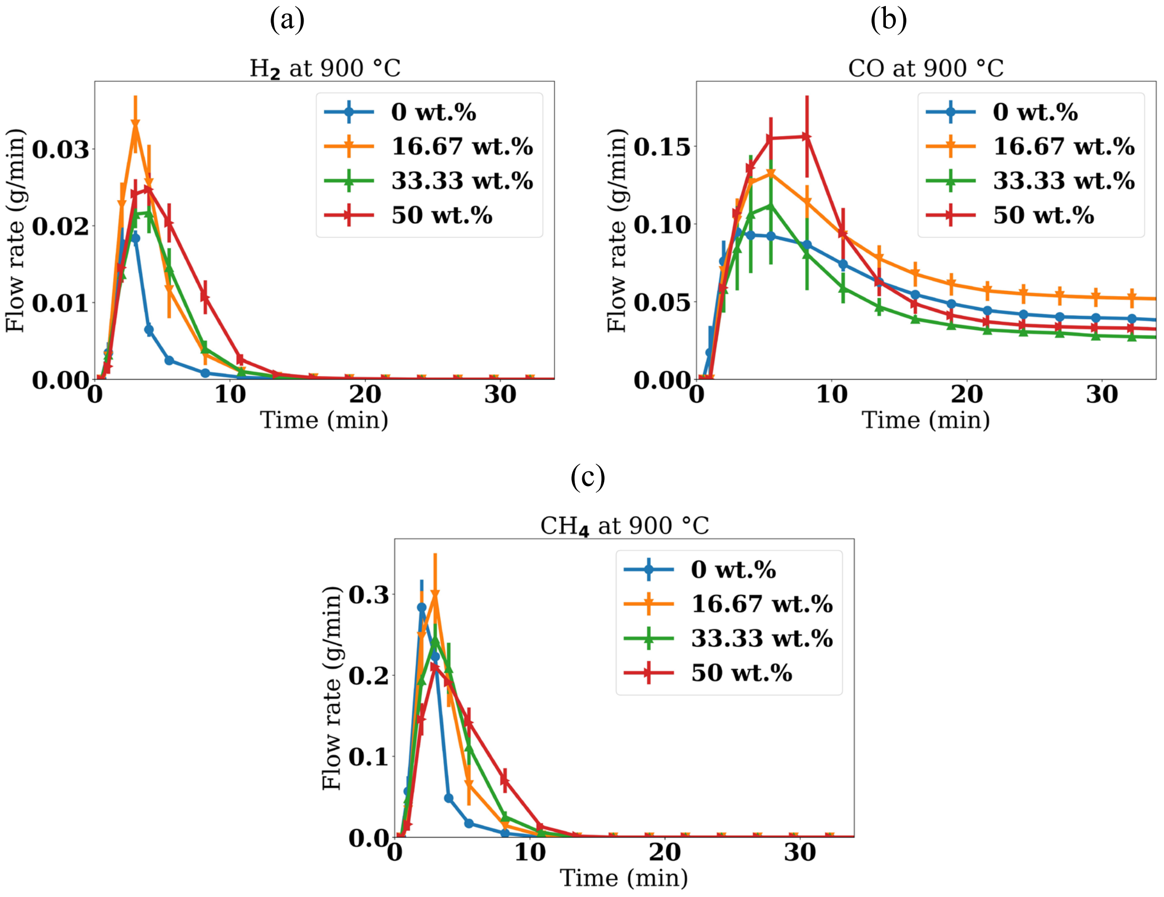

Figure 5.1. Effect of gypsum concentration on the evolution of syngas components (a) H_2, (b) CO, and (c) CH_4 with time

The reduction in peak height with an increase in gypsum proportions is mainly due to the heat-transfer limitations posed by gypsum addition resulting in the feedstock taking longer heating time [32]. At low gypsum amounts the quantity of gypsum was low enough not to cause such limitation and thus gypsum participated in the solid phase reaction much faster so that hydrogen evolution occurred earlier that provided the highest peak. However, at high gypsum proportions, the increased availability of gypsum increased the time for waste tires to react with gypsum and produce more H_2 over a longer time duration. While the above shows that gypsum interaction can be correlated with increased H_2 evolution, due to the oxidative potential of gypsum towards reductive gases such as H_2, the addition of gypsum was initially expected to decrease the H_2 output. This contradiction in the observed results was also reported in our previous publications where addition of gypsum to MSW gasification was found to increase H_2 and CO_2 yields [32]. Since the only known reaction of gypsum/calcium sulfate with the formed H_2 is to reduce H_2 ($CaSO_4 + 4H_2 \rightarrow 4H_2O + CaS$), the current results point to the interaction of gypsum with the reacting solid/melt-phase feedstock leading to an indirect rise in H_2. But an interesting observation was that gypsum incorporation leads to improved carbon conversion, and lowered char without compromising H_2 output. This interaction can be from the oxygen or the hydration present on the gypsum leading to increased oxygen availability for the reacting solid phase which leads to increased reforming and thus a rise in H_2. While it can be assumed that this rise in H_2 could be from the catalytic activity of gypsum, previous studies comparing the catalytic capabilities of different calcium compounds revealed no catalytic activity in sulfates [37]. So, improved reforming of waste tires from increased solid-phase oxygen availability via gypsum addition is the cause for the H_2 rise. Thus, the changing behavior of H_2 evolution with time for different gypsum concentrations is a combination of solid-phase reaction and the increased heat capacity of the total mixture at higher gypsum content.

$$\mathrm{CaSO_4 + 4C \rightarrow CaS + 4CO} \qquad (1)$$

$$\mathrm{CaSO_4 + 2C \rightarrow CaS + 2CO_2} \qquad (2)$$

$$\mathrm{C + CO_2 \leftrightarrow 2CO} \qquad (3)$$

$$\mathrm{CaSO_4 + 4CO \leftrightarrow CaS + 4CO_2} \qquad (4)$$

$$\mathrm{CaS + CaSO_4 \rightarrow CaO + SO_2} \qquad (5)$$

Figure 5.1(b) shows the effect of waste tires to gypsum feedstock ratio on the evolutionary behavior of CO. The results show that in all cases unlike the hydrogen evolution which was completed in 20 minutes, the CO evolution continued (but at a lower rate) to more than 50-minute time duration. This is attributed to the slow Boudouard reaction, shown in Eq. (3), at 900 °C. From 0-10 minutes, the CO evolution peak value increased with gypsum addition. The highest peak height was observed at 50 wt.% gypsum. This indicates a direct influence of gypsum in the decomposition of waste tires. The gypsum improves the reactivity of tires and reduces the formation of soot and tars as well as reduces char. The results indicate that the higher the gypsum proportion means more tire consumption. However, after 10 minutes, the peak decreased quickly in the presence of 50 wt.% gypsum compared to 0 wt.% gypsum case. At 50 wt.% gypsum proportion a sharper reduction in CO peak can be seen compared to the 33.33 wt.% and 16.67 wt.% cases. We infer that initially in the first 10 minutes, there was sufficient gypsum for reactions in Eq.(1,2) to proceed simultaneously, however, with the increase in CO, reaction shown in Eq. (4) is favored which consumes the CO. The depletion of gypsum after 10 minutes reveals that the CO evolution from then on depends on the Boudouard reaction, which is slower since most of the reactive components and volatiles are released in the first 10 minutes. Amongst the cases examined, the low gypsum proportion case of 16.67 wt.% showed the highest CO evolution in the char-gasifying zone while 50 wt. % showed the highest pyrolytic CO yield and CO for 33.33 wt.% was close to but earlier than 0 wt.% case. The varying levels of CO evolution with gypsum addition for the pyrolytic and char gasifying regions reveals that the CO evolution cannot directly increase with gypsum addition in CO_2-gasifying conditions due to different competing reactions of evolution and consumption of CO and CO_2. As the reaction progresses, the gypsum to carbon ratio increases, especially for high initial gypsum, leading to more CO_2 producing. Further discussion of CO and CO_2 relation will be discussed later in the section.

Figure 5.1(c) showing the influence of gypsum addition on the evolutionary behavior of CH_4 reveals that for all cases, CH_4 evolution was complete within the first 15 minutes. The presence of gypsum lowed the evolution peak height due to the heat-transfer limitations caused by increased mass but the overall CH_4 evolution seems to increase over time due to the long interaction of gypsum with the waste tire. This shows the influence of gypsum in the decomposition of tires, which suggests that adding gypsum promotes gasification since the higher-forming hydrocarbons are prevented from forming char and soot through reaction with gypsum. Therefore, gypsum effectively improves the reforming of waste tires and decomposes char and tar into non-condensable light hydrocarbons.

5.3.2 Effect of gypsum on cumulative yields of solid residue and product gases

From the gasification tests, the solid residue after gasification for 1hr was removed from the reactor, cooled and its weight measured to obtain its yields for all the cases. For easier understanding, the solid residue yields were normalized with respect to their corresponding initial mass of the waste tire and gypsum mixtures. The flow rates of syngas components measured with respect to time were also utilized to integrate over the reaction time to obtain cumulative yields. The aggregate of these cumulative yields including the output CO_2 was calculated as the product gas output and normalized with respect to the initial feedstock mass (only waste tire since it is the source for most of these gases). Figure 5.2 reveals the impact of initial gypsum concentration on the solid residue and cumulative product gas output yields. It is to be noted that the product gas reported here includes the CO_2 and a significant portion of this contributed from unreacted CO_2 we added for gasification while some CO_2 was produced from the gasification. This was carried out to observe the gypsum's impact on the net gas output, and since the integration time and the input CO_2 flowrates were same for all these cases, they can be compared. The figure reveals a clear increase in gas formation with gypsum addition and thus improves carbon conversion. Higher gypsum concentrations led to increased gas yields due to both improved reforming along with reactions with the char. All gypsum-char reactions result in increased gas products and thus leading to this behavior. While it may improve the carbon conversion, the syngas quality still needs to be verified since gypsum can contribute to increase in carbon conversion by just increasing CO_2 which can lower the syngas quality or its heating value. Figure 5.2 also shows that solid residue effectively increased from 30% to 40% as the gypsum increased from 0 to 50 wt. %. The solid residue from gypsum addition was off-white to yellow in color while the char from waste tires was obviously black. From this we can consider that addition of gypsum led to almost complete conversion of the waste tires and the solid residue is from the reacted gypsum products. Under this consideration, if we subtract the solid residues from waste tire alone from the solid residues from waste tires and gypsum gasification and normalize with respect to the added gypsum mass, we obtain the conversion of gypsum into gas-phase to be 46%, 50% and 49% for 16.67, 33.33, and 50 wt.% gypsum respectively. With the error limits, these values are close to each other, and it reveals that no matter how much gypsum was added the net conversion of the added gypsum was same. It means that as more gypsum is added more waste tire intermediates react with the gypsum and this also proves that the gypsum not only reacts with the char but also the reforming solids and volatiles.

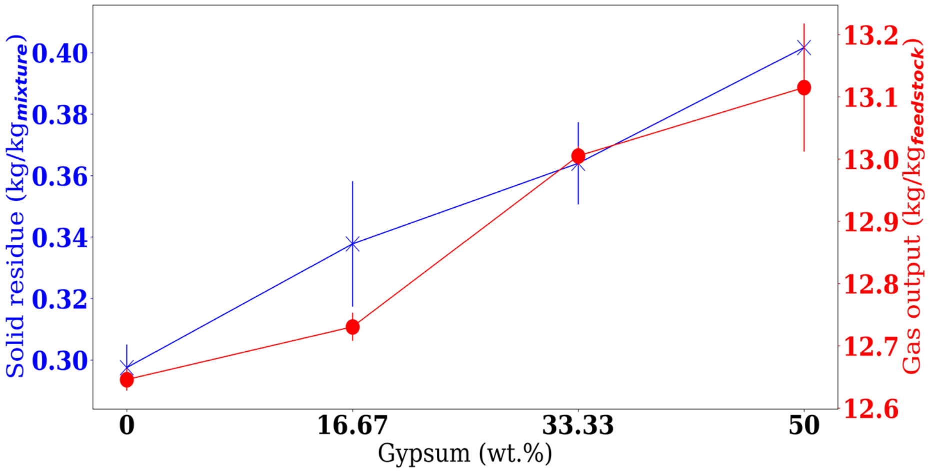

Figure 5.2. Effect of added gypsum concentration on the solid residue (including the reacted gypsum) and gas output from CO_2-gasification of waste tire gypsum mixtures (kg$_{mixture}$= mass of waste tire+gypsum; kg$_{feedstock}$=mass of waste tire; gas output= yields aggregate of H_2, CH_4, CO, CO_2 (including the added CO_2), C_2)

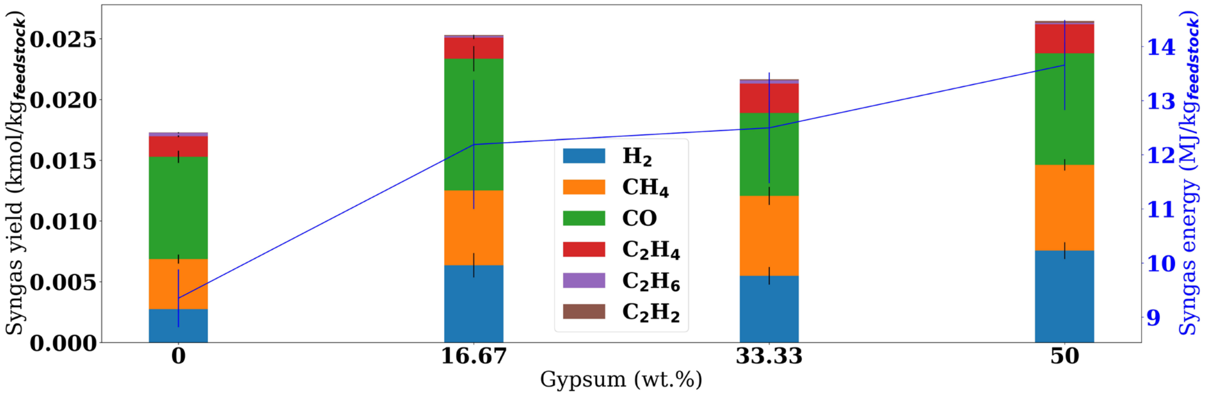

Figure 5.3. The cumulative yield of syngas (bar plot) and energy yield (line plot) with different amounts of gypsum addition (here kg$_{feedstock}$ refers to mass of waste tires only)

Figure 5.3 shows the influence of gypsum on the cumulative yields of individual syngas components and the calorific energy output in the form of syngas. It shows that the presence of gypsum improved the oxidation potential of the feedstock by increasing all components of the syngas (CO, CH_4, and H_2). Figure 5.3 shows that the cumulative yield of H_2 doubled and that the syngas energy yield (MJ/kg feedstock) increased by up to about 40% with gypsum addition. The effect of different amounts of gypsum additions to waste tires shows that the 50 wt% gypsum proportion (10gm WT:10gm gypsum) achieved the highest yield of H_2 as well the highest energy of the overall syngas. The 33.33 wt. % proportion (10gm WT: 5gm gypsum) had the similar energy yield compared to the 16.67 wt.%. These results show that gypsum addition in waste tire gasification enhances the H_2 and CH_4 yields for all cases and C_2 yields for high gypsum concentrations. This reveals that gypsum can be added to waste tire gasification without the need for changing operating conditions [32]. It also shows that 16.67 wt.% gypsum addition increased the yield of CO by almost 30% whereas adding 50 wt.% increased the yield by almost 10% as compared to CO_2-assisted gasification only. The net decrease in CO yield in the 33.33 wt.% case is caused by char reacting with gypsum to form CO_2 instead of CO. For the individual mass proportion, the highest yield and energy of the syngas were achieved with 50 wt.% gypsum addition to waste tires. Note that, even with the increased oxidation of feedstock, the H_2 fraction in the syngas was not affected by gypsum addition, as it showed a rather increasing tendency. This indicates the beneficial aspects of gypsum incorporation into waste tire feedstock with improved carbon conversion and lower char production without compromising H_2 production. The results presented here show that carbon conversion, energy and H_2 yields can be improved by incorporating gypsum in waste tires while the CO yields can be increased for certain controlled gypsum concentrations.

To probe further into the impact of gypsum concentration on the CO and CO_2 yields in a comparative mode, we calculated the differences of CO and CO_2 yields from waste tire and gypsum mixture gasification with respect to the yields from gasifying waste tires alone. From above, although gypsum addition led to increased H_2 and hydrocarbon yields for all the cases compared to gasifying waste tires alone, its impact on CO evolution is convoluted and correlated with the CO_2 evolution. Since the CO_2 change in Fig. 4 are differences with respect to waste tire gasification in similar conditions of CO_2 input, the shown results point to the additional CO_2 evolved from the addition of gypsum. It shows that at low gypsum concentration, additional CO_2 yield was minimal as the CO evolution reactions from Eq. (1-5) are favored according to the high temperature equilibrium. But at higher gypsum concentrations, increased CO_2 yields are unavoidable due to further reforming of waste-tires into high CO_2 yields. Even though CO_2 yields increased, they were compensated by the rise in H_2 and CH_4 yields effectively to avoid any drop in syngas energy output and this proves the viability of incorporating gypsum into waste tire gasification for improved reaction conversion.

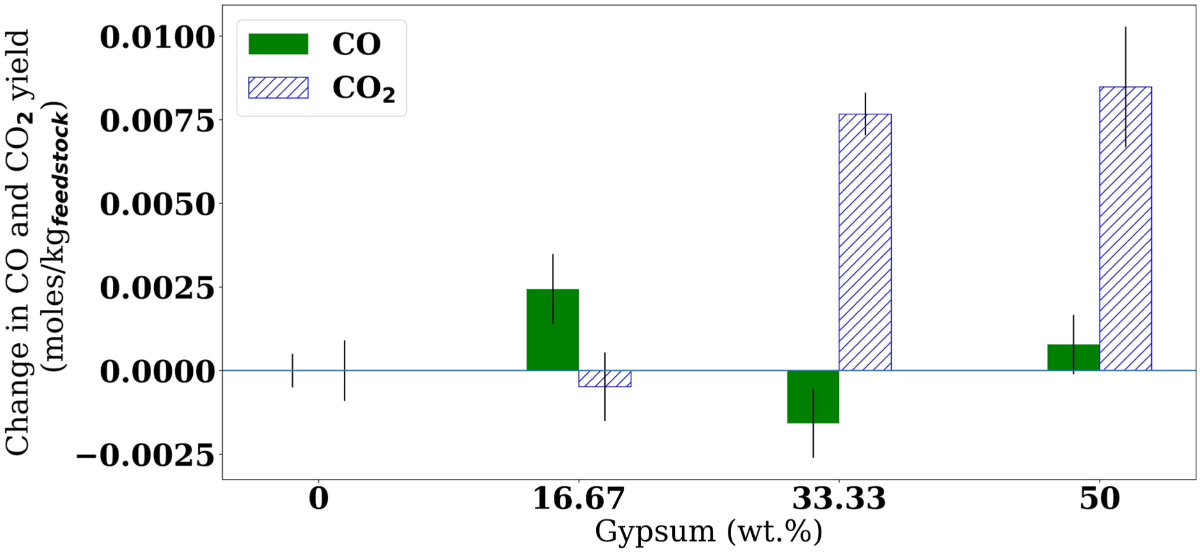

Figure 5.4. Effect of added gypsum concentration on the change in cumulative CO and CO_2 yields with respect to the CO_2 gasification of waste tires with no added gypsum ($kg_{feedstock}$= mass of waste tire).

5.3.3 Effect of gypsum on sulfur evolution

While the above results show that gypsum addition can improve gasification output, a potential disadvantage exists in the form of added sulfur to the system. So, it is important to investigate the fate of gypsum sulfur during gasification to identify if viable conditions exist to ensure this added sulfur does not leave in the gas form and thus contaminate syngas. For this, Aspen Plus® was used to conduct thermodynamic equilibrium analysis and examine the effect of temperature and gypsum mass proportion on sulfur transformation. A feed rate of 100 kg/hr of waste tires was used as a basis for all the calculations. The CO_2 flow rate was fixed at 5 times the number of waste tires while gypsum was varied from 0 to 100 kg/hr. The ultimate analysis used was obtained from Mavukwana et al., 2021. For 100 kg/hr of tires, 53 mol/hr of S enters the system while for every 100 kg/hr of gypsum, 734 mol/hr of S enters the system.

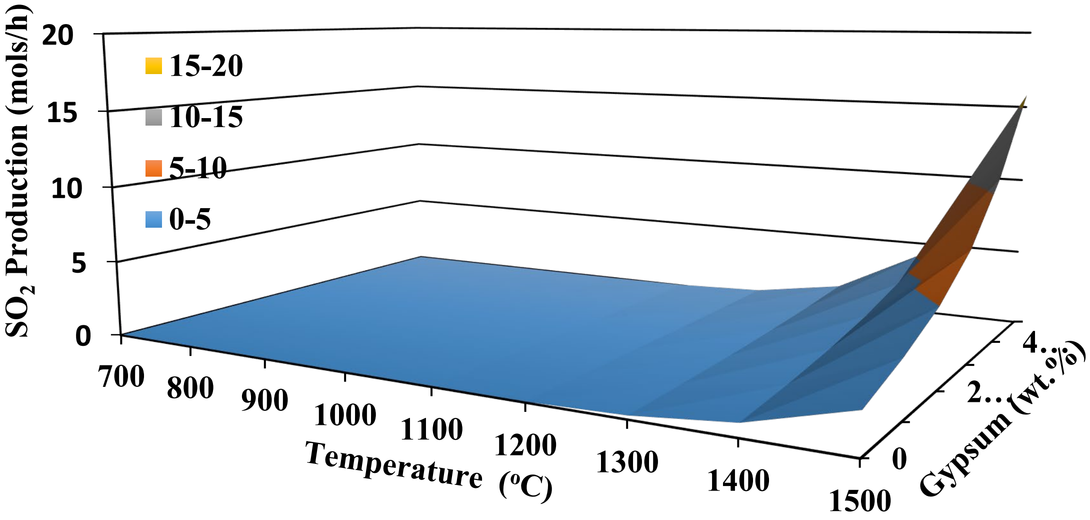

Figure 5.5. Effect of temperature and gypsum on SO_2 production.

Figure 5.5 shows the effect of temperature and gypsum on thermodynamic equilibrium SO_2 output from CO_2-gasifying waste-tires with gypsum. The result in the figure shows that for waste tire-gypsum mixture in a CO_2 atmosphere, the gasification should be conducted at temperatures lower than 1200 °C to prevent the conversion of sulfur to SO_2 gas phase. At a high mass gypsum addition of 50 wt.%, only 2% of the total sulfur that entered the system was transformed into SO_2. This suggests that the SO_2 produced here was coming from the sulfur in tires and not from gypsum. Thus, gasification of waste tires with gypsum at temperatures below 1200 °C, can provide with the advantageous improvement in energy yields and carbon conversion without any further syngas contamination with sulfur products such as SO_2.

5.3.4 Comparison with feedstocks

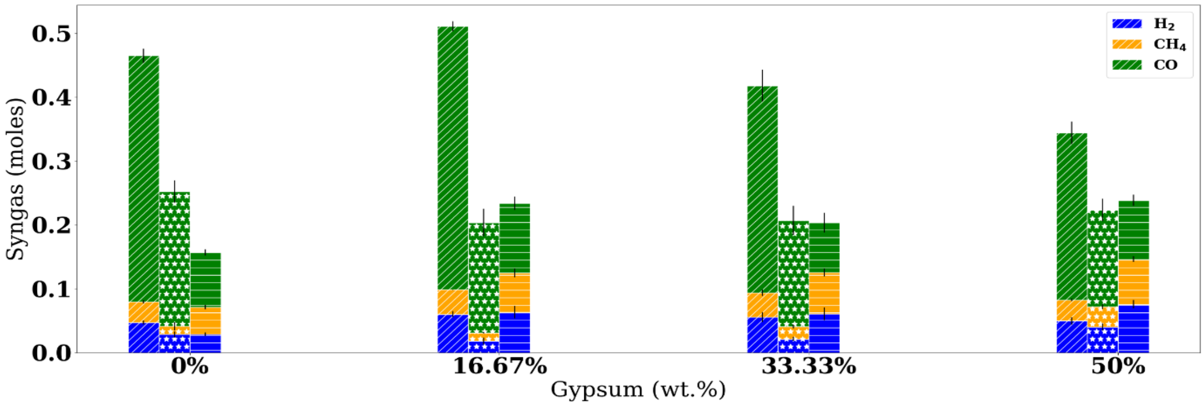

Figure 5.6. The yield of syngas from wood (//), PET (*), and Waste tires (-) with different amounts of gypsum addition.

Figure 5.6 shows a comparison of the co-gasification of waste tires with gypsum to that of the co-gasification of wood and PET with gypsum in a CO_2 atmosphere. In Figure 5.6 wood biomass provided a higher yield of syngas when compared to waste tires and PET mixtures. The yield of CO dominated the syngas mass yield in all feedstocks. The CO mole fraction in syngas dominated due to the Boudouard and hydrocarbon reforming reactions that occur in the CO_2 gasification atmosphere. However, in wood, the high oxygen content in the wood leads to decarboxylation from the organic structure which contributes to the high yield of CO. Waste tires ad PET have minimal oxygen content. Equally waste tires have more fixed carbon than wood whereas PET plastics contained no fixed carbon (FC). This fixed carbon reacts slowly with CO_2 to form CO once all the volatiles are released. Therefore, the feedstock component with the high FC showed decreased yields of CO because the gypsum gets consumed earlier before activating the char in waste tires as compared to wood. For PET, the volatiles is released with minimal interaction with gypsum. At higher gypsum proportions, the volatiles interacts with gypsum to reveal the observed increase in syngas yield with increased gypsum for the PET case.

At low gypsum proportions (16.67 wt.%), the overall syngas yield increased in wood and tires while it showed a decrease for the PET case. When gypsum is increased to 50 wt.%, the syngas yield deceased from the wood while it increased from the waste tires and PET. With wood, the oxidation levels increased such that the syngas components were oxidized thus decreasing the yield when the gypsum ratio decreased to 16.67 wt.%. Wood contains more oxygen than tires and PET, therefore in the same condition, there will be more oxidation in wood than that in tires and PET. Therefore, gypsum addition offers an advantage to waste tires and PET gasification over woody biomass feedstock.

5.4 Conclusions

Experimental results on the synergetic potential of incorporating waste gypsum into the gasification of waste tires showed that gypsum addition improves the conversion of waste tires to syngas. The yield and quality of syngas increased with the addition of gypsum along with carbon conversion. The overall cumulative yield increased by 55% and the syngas energy yield increased by 40% when 50 wt.% gypsum was added. Gypsum conversion was about 50% irrespective of the amount of gypsum added. While gypsum addition improved reforming of waste tires to obtain more H_2, CH_4 and hydrocarbons, its impact on CO yield compared to waste tire gasification alone was dependent upon the amount of gypsum added. Low gypsum addition improved CO in the form of partial oxidation while further increasing led to significant rise in CO_2 yields. Thermodynamic equilibrium analysis using Aspen Plus also showed that adding gypsum did not increase the production of SO_2 for temperatures below 1200 °C. These results reveal that gypsum can be incorporated into waste tire gasification to improve syngas yield and uniformity. These results, therefore, provide a new potential for synergistic disposal of low-value wastes which can improve the techno-economic viability of energy and material recovery from waste tires.

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6 Analysis of power generation from waste tires: Processes synthesis

Publish research article

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Short summary

In the previous chapters, it was shown that through gasification waste tires can be converted to various chemicals and power. In this chapter 4, we consider waste tires as the fuel source to produce electricity. Waste tires are a good source of carbon and hydrogen and with a low ash material and a heat value comparable to coal and biomass, tires are a perfect source to produce power. In this study, we apply previously developed process synthesis techniques to find and analyze the performance limits for the conversion of the waste tire to electricity. Three possible routes are analyzed (1) direct combustion (2) internal combustion engine driving a generator and (3) the integrated gasification combined cycle (IGCC). The fundamental laws of thermodynamics, as well as the conservation of mass, are used as high-level synthesis tools to identify optimal targets for power production from waste tires from a system and equipment level. Two quantities, thermal efficiency and work efficiency are used to compare the performance of the three power plants routes. In Chapter 3, we have shown that for every chemical transformation process, defined by any mass balance, there are two aspects of energy requirements associated with it, which is the change in enthalpy (ΔH) across the process boundary and the quality of the energy expressed in terms of the equivalent amount of mechanical work (or simply referred to as 'work') required to effect the change from feed to the product (ΔG). The heat requirements of a process will only meet the work requirements of a process if the heat is supplied or released at one unique temperature, termed the Carnot temperature. Since for most processes, the Carnot temperature may not be feasible, such that the process would need to operate at a different temperature other than the Carnot. The work

transferred to a process when the heat is supplied at a temperature other than the Carnot translate to the work loss or work deficiency on the part of the process. In this chapter, we use these principles to evaluate the best route for the conversion of tires to electricity.

The results show that the IGCC system can conserve the chemical potential of waste tires. IGCC system developed here does not use oxygen or air during gasification and achieved a thermal efficiency of 45.65 % with a net-work output of 10.5 GJ/ton of tire which is much higher than that of conventional coal IGCC at 9.6 GJ/ton of coal.

Declaration by canditate:

The scope of my contribution to the chapter is as follows:

Planning simulation	70%
Conducting the simulation	100%
Results interpretation	80%
Compilation of the chapter	100%

The following co-authors have contributed to this chapter as per following:

Co-author	Nature of contribution		Contact and signature
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	Results interpretation	10%	
	Revision of chapter	40%	
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	Results interpretation	10%	
	Revision of chapter	60%	

I declare that the above information is true and reflects the nature and extent of the contributions of the candidate and the co-authors

Signature of candidate:……………………..

Date:…………………….

Thermodynamics analysis of waste tire power plants

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Abstract

Waste tire generation in South Africa is an issue for which no sustainable solution has been found. South Africa generates over 177 385 tons of waste tires per year and only around 25% is recycled, the remaining 75% accumulates in storage depots, and landfills across the country. In this work, a slurry-fed IGCC system is analyzed. This system does require the use of oxygen and is designed to be self-sustaining and produces electrical power. A sensitivity analysis shows that considerable gains in thermal efficiency are made by using a turbine pressure ratio of between 20 and 30 bar. This data was then used to develop a system that processes 518 tons/day of waste tires and operates at a gas turbine pressure ratio of 30 bar and a 1600 ºC combustion temperature. The net power production from the system is 89 MW, with a thermal efficiency of 45.65% and a work efficiency of 44.97%. However, the results from Aspen Plus were significantly less than predicted with an overall net efficiency of 32 %. Despite the discrepancy waste tire IGCC net-work output was found to be 10.5 GJ/ton of tire much higher than that of conventional coal IGCC at 9.6 GJ/ton of coal.

Key words: Waste tires; thermodynamic analysis; IGCC; aspen plus; thermal efficiency

6.1 Introduction

To address the challenge of waste tires in South Africa, a process that can consume the total waste tire accumulation need to be developed. Current processes (re-treading, incineration, crumbing, and pyrolysis) are limited to 40-60 tonnes/day due to environmental concerns, high energy cost, low market value, and more crucially low product demand. These concerns limit the development of the current methods of recycling tires on a commercial scale. The considered process must process over 500 tonnes per day to address the challenge; however, it must be self-sustainable and generate profit.

Due to the high combustibility of waste tires, it is not surprising that moves are afoot to harness this energy. Life cycle assessment studies show that waste tire thermal conversion processes are the most economical, have the least environmental impact and are self-sustainable. Corti and Lombardi [1] showed that from an investigation of the total energy and raw material balance waste tire combustion had more advantages than the other means of managing rubber wastes in that preparing tires as an alternative fuel requires a smaller financial and energy outlay than their recycling by grinding, which is an energy-consuming process [2,3]. Therefore, converting tires to electrical power generation is one area where tire re-use could be self-sustainable and profitable. Currently, the South African electricity grid is strained, and the country is seeking to invest in alternatives, including waste to energy process to increase the generating capacity. Therefore, converting waste tires will address the disposal problem as well as the energy challenges the country has.

The combustion of tire derived fuel (TDF) to produce power can be done in three ways. (1) Direct combustion to produce heat to generate steam, (2) TDF gasification for electric and thermal power generation, from syngas combustion in an internal combustion engine driving a generator or (3) in a gas turbine driving a generator [4,5]. The latter is the integrated gasification combined cycle (IGCC), which has become the cleanest and efficient method to power generation and chemicals production. In the IGCC set-up, a carbonaceous material is gasified to produce syngas, a mixture of hydrogen and carbon monoxide, which when cleaned of harmful substances is combusted in a gas turbine at high temperatures. The exhaust gas from the turbine is sent to a heat recovery steam generator to produce steam, which is then passed in a steam turbine to produce more power. The IGCC is advantageous in that the sulfur and nitrogen compounds are captured and not discarded to the environment.

The intention of this study is to apply previously developed process synthesis techniques [6-8] to find and analyse the performance limits for the conversion of the waste tire to power. In particular, the objective is to identify an optimum target for the conversion of the waste tire to power and then develop a flowsheet that would perform as close to the target as possible. Two quantities, thermal efficiency and work efficiency will be used to assess the performance of the power plants. Thermal efficiency is the ratio of the actual amount of work produced over the amount of heat supplied to the heat engine. The work efficiency is the measure of how much real work is recovered from the maximum amount available. The maximum amount of work available is given by the change in Gibbs free energy between the feed and the product streams. Hence, work efficiency can also be called the second law efficiency [7]. To verify the feasibility of the limit of performance, an Aspen Plus® simulation of the synthesised flowsheet is also developed.

This work will be unique to others already published in the field in that a system analysis approach is used to determine the limits of performance of the process in terms of the material going in and out of the process as well as the energy, both in quantity and quality, involved in the transformation. This provides the theoretical knowledge which could be used to decide whether it is worthy to develop a process to convert waste tire to power.

6.2 Methodology

The fundamental laws of thermodynamics, as well as the conservation of mass, will be used as high-level synthesis tools to identify optimal targets for power production from waste tires from a system and equipment level. The approach is drawn from the work of Patel and Sempuga [9–11] who showed that three basic fundamental tools which are mass, heat, and work could be used to synthesise more efficient chemical processes. In their previous works, these authors have shown that for every chemical process, defined by a specific material balance, there are two aspects of energy requirement associated with it. These are the amount of energy and quality of that energy. It can be shown that the amount of energy requirement (input or output) is given by the change in enthalpy (ΔH) across the process boundary. The quality of the energy is expressed in terms of the equivalent amount of mechanical work (or simply referred to as 'work') required to effect the change from feed to the product. It can be shown that for processes where the feed and product streams are at a reference temperature and pressure, the work requirement is given by the change in Gibbs free energy between the feed and the product stream.

For processes where energy is transferred in the form of heat alone, then the minimum (or maximum) work requirement is given by Eq. 1, which states that the heat requirements of a process will meet the work requirements of a process if the heat is supplied or released at one unique temperature, termed the Carnot temperature.

$$\Delta G_p^o \ (T_o, P_0) = \Delta H_p^o \ (T_o, P_o)\left(1 - \frac{T_o}{T_{carnot}}\right) \text{eq. 1}$$

$$W_p(T_H) = \Delta H_p(T_o, P_o)\left(1 - \frac{T_o}{T_H}\right) \qquad \text{eq. 2}$$

Where ΔG^o_p and ΔH^o_p are Gibbs free energy and enthalpy at standard temperature and pressure, T_{carnot} is the Carnot temperature, and T_o is the reference temperature. Such a process will not lose or take additional energy to the environment. However, for many processes, the Carnot temperature may not be feasible, such that the process would need to operate at a different temperature (T_H) other than the Carnot, and this leads to process irreversibility. The work transferred to a process when the heat is supplied at a temperature other than the Carnot temperature is calculated using eq. 2. The difference between eq.2 and eq.1 translate to the work loss or work deficiency on the part of the process. The authors have shown that this approach can be used to set performance targets and identify opportunities for innovation at the early stage of the design well before the flowsheet is developed.

6.2.1 Estimation of thermodynamic properties

The approach employed in this study needs two thermodynamic properties, i.e., the enthalpy (ΔH) and the Gibbs free energy (ΔG), and together with the molecular formula of a waste tire.

However, tires do not have known thermodynamic properties and molecular structure, since they are a mixture of polymers, plasticisers, metals, and other inorganic substances in varying quantities. To simplify the work, the waste tires are treated as a single chemical compound rather than a mixture. The ultimate and proximate analysis of tires shown in Table 6.1 are used to determine the empirical formula of a single molecule of a passenger tire, enthalpy and the Gibbs free energy [12] .

Table 6.1. Ultimate analysis of waste tires [12].

Ultimate Analysis wt.%		Proximate Analysis wt.%		
C	85.05	Moisture	1.14	
H	6.79	FC	32.28	
N	0.5	VM	62.24	
O	1.75	ASH	4.35	
S	1.53	LHV	34.9	MJ/kg

The empirical formula for waste tires can be derived from the ultimate analysis in Table 6.1 of a passenger tire with the metals and reinforcement fabric removed, is represented as: $CH_{0.95}O_{0.02}N_{0.005}S_{0.007}$.

The heat of formation was calculated to be $\Delta H^{o} = -59.77\ kJ/mol$ from the LHV of the waste tires whereas the Gibbs free energy at standard temperature and pressure was estimated to be $\Delta G^{o} - 47.78 kJ/mol$ using the method described in Prins [13].

6.3 Results and discussion

6.3.1 Power plant analysis

Direct combustion

Let us consider a simple process for the combustion of tires to produce power, as shown in Figure 6.1. The assumptions are that the feed enters the process at ambient conditions (25 ºC and 1atm), and the products also leave the process at ambient conditions. A reversible heat engine is used to recover the work by using the heat produced during combustion. The total amount of energy that the process is capable of delivering is given by the change in enthalpy (ΔH) between the feed and the products streams. The negative value indicates that the process will release energy. It can be shown that the maximum amount of work that can be recovered from the process is given by the change in the Gibbs free energy. The negative ΔG indicates that the process has the potential to produce work. Both quantities are calculated at ambient temperature and pressure. The process in Figure 6.1 considers a case where only heat is used to recover the work potential of tires. For this manuscript, the term "work" refers to the mechanical energy that can be produced.

The Carnot temperature for the process, according to "eq.1" is:

$$T_{carnot} = \frac{T_0}{\left(1 - \frac{\Delta G_p{}^0}{\Delta H_p{}^0}\right)} = 13645.71\text{K}.$$

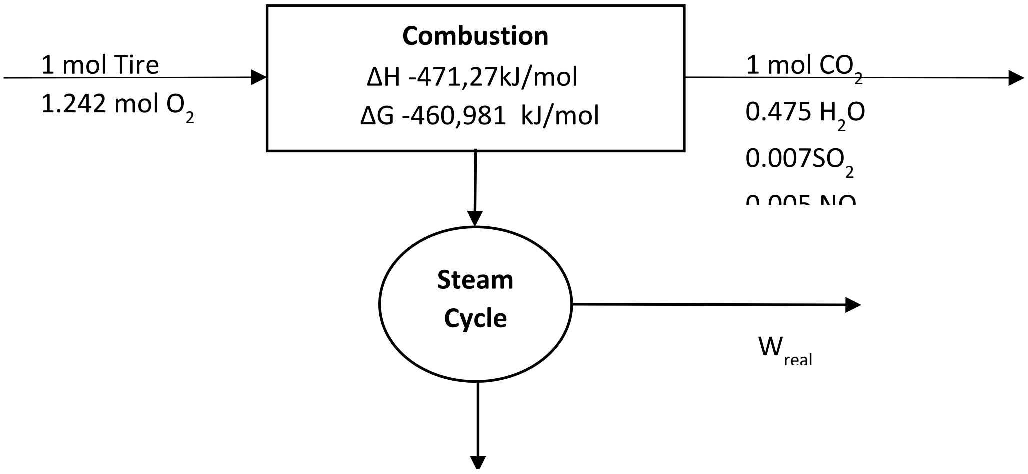

Figure 6.1. Systems-level representation of a waste tire fired power plant.

Hence, to recover the work potential of waste tire combustion, a reversible steam cycle system must be able to absorb heat at a temperature of 13645.71 K (13372.71°C) and reject the heat to the environment at 25 °C. Most power plants use steam cycles to recover the work potential of tire combustion. Due to metallurgical limitations, it is not possible to generate steam at temperatures equivalent to Carnot temperature of combustion. Advance power plants are capable of operating at the insurmountable temperature threshold of 700 °C, which is a significantly lower temperature than the Carnot. Suppose such metallurgical equipment is used, the work that can be recovered by the heat engine will be significantly lower than the maximum available potential, consequently reducing the efficiency of the power plant. The real work achievable for the system in Figure 6.1 using steam at 700 °C is:

$$W_{real} = \Delta H_p^o \left(1 - \frac{T_0}{T_{SC}}\right) = -471.27 \left(1 - \frac{298}{973}\right)$$

$$= -326.94 \; kJ/mol$$

The work efficiency of the process becomes:

$$\eta_{work} = \left(\frac{W_{real}}{\Delta G_P{}^o}\right) \times 100 = 70.92\%$$

Whereas the thermal efficiency is:

$$\eta_{thermal} = \frac{W_{real}}{\Delta H_P^o} \times 100 = 69.37\%$$

These values represent the maximum efficiency for a waste tire power plant using the mentioned conditions. The values assume that the heat is rejected to the environment at 25 °C. However, in real processes heat losses take place at higher temperatures through the exhaust gas and equipment. Steam in the heat engine cycle is condensed at much higher temperatures. A steam cycle which rejects heat at 100 °C and 1atm, the work efficiency decreases to 63.04% and thermal efficiency to 61.66%. For a real process with heat loss through equipment, the efficiencies could even be 40% or even less.

Gasification and syngas combustion

Direct combustion of tires is limited to 70.92% work recovery. Another approach is to employ chemical routes (splitting the combustion into multiple steps) that allow the work potential of tires to be reached more efficiently and at lower temperatures. To further increase the efficiency of power generation, waste tires can be converted to syngas through gasification, then the produced syngas is combusted either in an internal combustion engine driving a generator, or combustion chamber from which heat generated is recovered using a steam cycle, or alternatively the syngas can be burned in a combined gas turbine and steam cycle system [7]. The following section explores all three methods.

Syngas combustion to generate steam

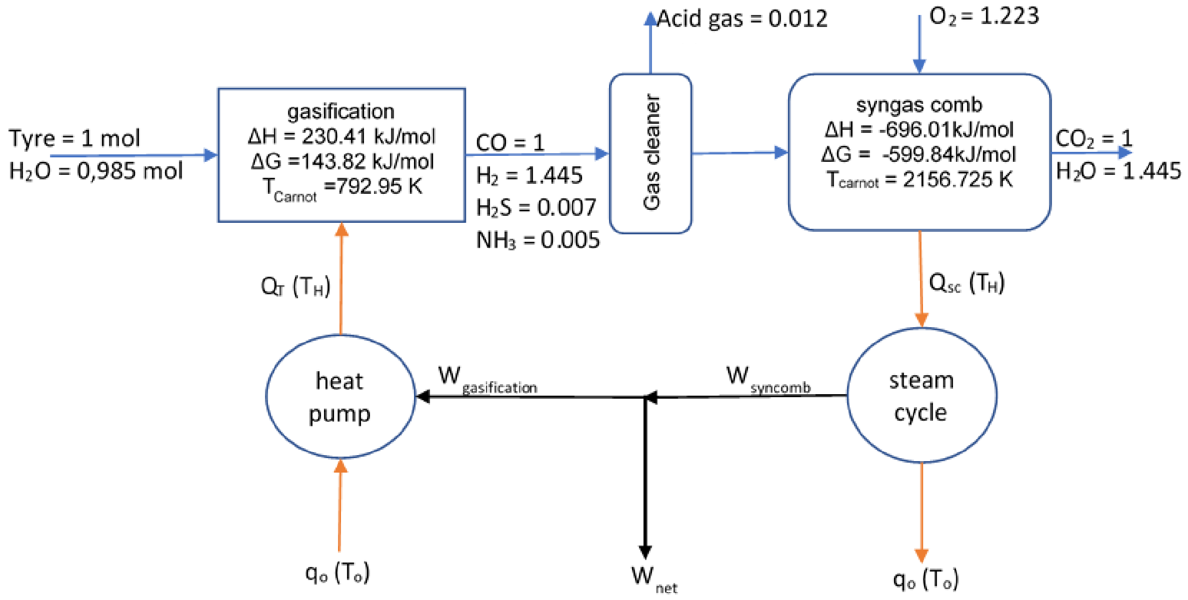

Figure 6.2. Power generation via syngas combustion.

In Figure 6.2 the tires are gasified using water to produce syngas, the syngas is cleaned off nitrogen and sulphurous gases and burned in a combustion chamber. To reach maximum efficiency, both units are assumed to operate at their Carnot temperatures and an I deal gas cleaner is assumed. In Figure 6.2, the gasification step is shown to be an endothermic process; therefore, a heat pump is used to draw heat from the environment to supply the process. Since the gasifier is operated at its Carnot temperature, the work supplied to the heat pump will be equal to the Gibbs free energy of the gasifier. A steam cycle is used to recover the heat generated in the syngas combustion chamber. The steam cycle is taken to operate at 700 ºC, which means the heat transfer across the chamber takes place at a lower temperature than Carnot. The work recovered from syngas combustion is:

$$W_{syncomb} = \Delta H_p^o \left(1 - \frac{T_0}{T_{SC}}\right) = -696.01 \left(1 - \frac{298}{973}\right)$$

$$= -482.84\ kJ/mol$$

The work required by the gasifier is:

$$W_{syncomb} = \Delta H_p^o \left(1 - \frac{T_0}{T_{gasifier}}\right) = 230.41 \left(1 - \frac{298}{792.95}\right)$$

$$= 143.82\ kJ/mol$$

Therefore, the net-work produced by the process is:

$$W_{net} = W_{gasifier} + W_{syncomb}$$

$$= 143.82 + (-482.84)$$

$$\therefore W_{net} = -339.022 kJ/mol$$

The work efficiency of the process becomes:

$$\eta_{work} = \left(\frac{W_{net}}{\Delta G_P{}^o}\right) \times 100 = 73.54\%$$

Whereas the thermal efficiency is:

$$\eta_{thermal} = \frac{W_{net}}{\Delta H_P^o} \times 100 = 71.94\%$$

This is the maximum possible work efficiency for a combustion process that produces liquid water and a gasification process that uses liquid water. For combustion processes producing gaseous water, the maximum work efficiency is 64%. For complete conversion of tires, the gasification temperature is often set at higher temperatures than the Carnot temperature. If the gasification is operated at 1300 ºC, the work and thermal efficiency of the process reduces to 64% and 62% for a process producing liquid water and the work efficiency reduces further to 55% when the process produces gaseous water.

Internal combustion engine

In this configuration the syngas from the gasification island is burned in an internal combustion engine driving a generator to produce electricity as well as thermal heat. The thermal heat could also be used for steam production. In an internal combustion engine, the gas is burned inside pistons.

The energy balance around the internal combustion is:

$$\Delta H_{process} = Q_{lost} + W_s$$

Where W_s is the quantity of mechanical energy transfer across the process and Q_{lost} is the heat lost or recovered when the engine is cooled using water of a refrigerant. Suppose the engine is cooled by generating steam at 700 ºC then the work transferred across the process would be the same as the of a combined cycle given by:

$$\Delta G_p^o(T_o, P_0) = \Delta H_p^o(T_o, P_o)\left(1 - \frac{T_o}{T_{Rev}}\right) + W_s\left(\frac{T_0}{T_{Rev}}\right) \qquad \text{eq.6}$$

Since the thermal heat is recovered at 700ºC, the work recovered through the generator will be -382.01 kJ/mol. This is the total work recovered by the process since there is no steam cycle. Therefore, the work efficiency of the process is 51.67% for a system producing liquid water and 74% for a system producing gaseous water. If we consider that gasification happens at 1300ºC, the work efficiency drops to 42% for a system producing liquid water and 64% for a system producing gaseous water.

The internal combustion engines (ICE) underperforms when compared to the combined cycle (IGCC), however since IGCC can be expensive to construct, the ICE offers an alternative solution. The following section focuses on the effect of operating parameters on the efficiency of the IGCC system.

Combined cycle

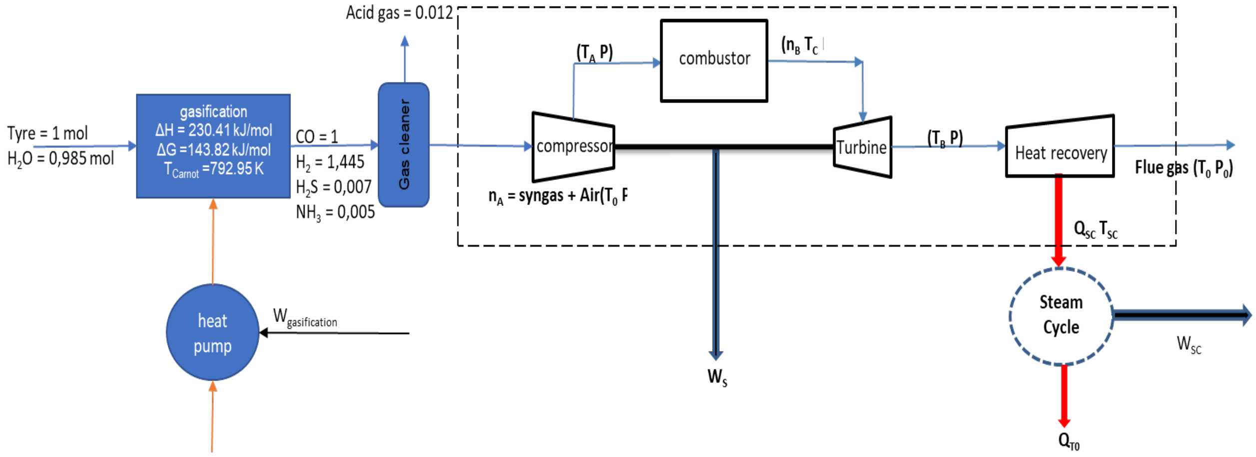

Figure 6.3. Combined Cycle Process.

In this section, let us consider the combined cycle. Figure 6.3 shows the basic schematic representation of what happens in a combined cycle. The syngas is combusted in a gas turbine, and the exhaust gas from the turbine is sent to a heat recovery steam generator to produce steam. The gasification step is assumed to be the same as the previous section, which showed the work required is 143.84 kJ/mol if the unit is operated at the Carnot temperature if the (792.95 K). In Figure 6.3, there is mechanical energy transfer (W_s), and there is a single heat transfer across the process (Q_{SC}). The energy balance across is given by:

$$\Delta H_{process} = Q_{sc} + W_s \quad \text{eq.5}$$

Where W_s is the quantity of mechanical energy transfer across the process and Q_{sc} is the heat recovered by the steam cycle. In the previous section, it was shown that Q_{sc} is a function of the temperature at which heat is recovered by the steam cycle. Therefore, one can see that the mechanical energy transfer across the process is also dependent on the temperature of the steam cycle. If the steam cycle operates at Tcarnot, then the work transfer across the process would be zero. The further away the operating steam temperature is from the Carnot temperature, the higher the amount of work that must be transferred across the process. Therefore, for a combined cycle process, the work requirement is given by:

$$\Delta G_p^o(T_o, P_0) = \Delta H_p^o(T_o, P_o)\left(1 - \frac{T_O}{T_{Rev}}\right) + W_s\left(\frac{T_O}{T_{Rev}}\right) \qquad \text{eq.6}$$

Where T_{Rev} is the reversible temperature at which the steam cycle must operate for the overall process to be reversible [7].

Thus, when W_s is zero, T_{Rev} would be equivalent to the Carnot temperature. Eq. 6 shows that W_s can be manipulated such that T_{Rev} is within achievable temperatures, thereby providing means for the work potential target to be reached at lower temperatures. This is the fundamental advantage of the combined cycle that the work target can be met at lower steam temperatures by manipulating the work recovered in the gas turbine. However, W_s depends on pressure. Therefore, pressure can be manipulated such that the work target is reached at a lower reversible temperature (Trev). In this analysis, we indicated that the steam cycle operates at 700 ºC. Therefore, if the heat transfer across the process happens at 700 ºC, using eq. 6 the shaft work (W_s) produced by the process would be -382.01 kJ/mol. From eq. 5 the Qsc is calculated to be -314.002 kJ/mol. using eq.2 the work generated by the steam cycle is thus -217.83 kJ/mol. Taking into consideration the work needed by the gasifier, the net-work produced by the process is -456.02 kJ/mol. Leading to a maximum work efficiency of 98.9% and thermal efficiency of 96.7% for a process producing liquid water. The values reduced to 96% and 94% when the process produces gaseous water. If the gasifier is operated at 1300 ºC, the maximum achievable work efficiency would be 87% and 85% thermal efficiency. Therefore, in comparison, the integrated gasification and combined cycle achieve greater efficiencies making the process better than other strategies. However, in a combined cycle, there are many parameters, such as turbine combustion temperature and pressure that influence the net efficiency of the process. The following section uses these fundamental concepts to investigate the effect of operational parameters on the process performance.

6.3.2 Sensitivity analysis: Waste Tire Integrated Gasification Combined Cycle (IGCC)

Figure 6.4 shows the ideal waste tire IGCC system. The first step is the gasification of waste tires into syngas. The Texaco entrained flow gasifier is selected for this analysis because they are versatile as they can use all type of carbonaceous feeds and operate at temperatures above 1000 ºC to ensure high carbon conversion and a syngas free of tars. The syngas is cooled with water to 30 ºC and then sent to an ideal cold gas cleaning unit (CGCU) to remove H_2S, NO_x, and CO_2. An Ideal cold gas cleaning unit is considered to examine the maximum efficiency. The cleaned syngas is mixed with a stoichiometric amount of air and combusted in an isentropic gas turbine to produce work. The exhaust gases from the turbine are sent to the heat recovery steam generator (HRSG) to produce steam that is used to produce more work.

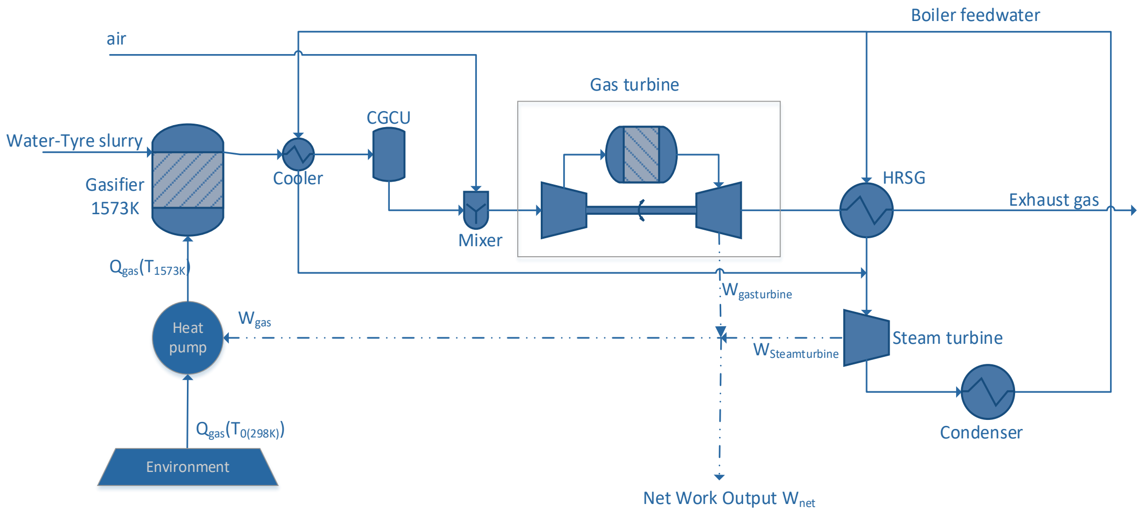

Figure 6.4. Ideal waste tire IGCC system.

The most critical parameters in an IGCC system analysis is the net-work output, thermal efficiency, gasification temperature, gas turbine combustion temperature, and emissions. These parameters are dependent on two variables, mainly the air flow and compression ratio in the turbine plus the type of gasification agent used. Gasification of tires yields three classes of products gases, char, and liquid. The yield of each product is a function of the temperature. Review by [14] showed that steam gasification of tires at 1000 ºC yields 5 wt% liquid products, 86 wt% gas products and the rest char. The authors reported that high temperatures reduced the production of soot and tars. For this work, the gasification temperature is set at 1300 ºC to ensure complete conversion of tires. The feed to the gasifier is a tire-water slurry. Oxygen is not used as an oxidant. The slurry concentration is estimated using the stoichiometric amount of water required in eq. 7. The work and heat requirements for this unit is to be supplied by the electrical power produced in the gas and steam turbines. The material balance for waste tire gasification using water as the oxidant can be written as follows:

$$C_1H_{0.949}O_{0.015}N_{0.005}S_{0.007} + 0.985H_2O = CO + 1.445H_2 + 0.007H_2S + 0.005NO_2$$

eq.7

Equations 8-17 taken from [7], are used to calculate the parameters of the waste tire IGCC system (Figure 6.4).

Gasification:

$$\text{Heat}\left(Q_{gasification}\right) = \Delta H^{o}_{gasificatio\,(T_O)} = \Delta H^{o}_{products} - \Delta H^{o}_{reactants} \qquad \text{eq.8}$$

Work $(W_{gasification}) = Q_{gasification}\left(1 - \frac{T_o}{T_H}\right)$ eq. 9

Turbine (isentropic):

$$T_{compresion} = T_o(P_{Ratio})^{\frac{\gamma-1}{\gamma}}$$

$$T_{combustion} = T_{turbexit}(P_{Ratio})^{\frac{\gamma-1}{\gamma}} \qquad \text{eq.10}$$

Work produced by turbine = $_{GT} = n_{in}\int_{T_o}^{T_{comp}} C_P\Delta T + n_{out}\int_{T_{comb}}^{T_{turbexit}} C_P dT$ eq.11

Heat Recovery Steam Generator (HRSG):

Heat absorbed = $Q_{HRSG} = n_{out}\int_{T_{turbexit}}^{T_o} C_P dT$ eq.12

Steam temperature = $T_{HRSG} = \frac{T_{turbexit} - T_0}{ln\frac{T_{turbexit}}{T_0}}$ eq.13

Work recovered = $W_{HRSG} = Q_{HRSG}\left(1 - \frac{T_0}{T_{HRSG}}\right)$ eq.14

Efficiencies:

Total Work $(W_{net}) = W_{GT} + W_{hrsg} + W_{gasi}$ eq.15

Work efficiency = $\eta_{work} = \frac{W_{net}}{\Delta G^0_{tyrecomb}(T_0)}$ eq.16

Thermal Efficiency = $\eta_{thermal} = \frac{W_{net}}{\Delta H^0_{combustion}(T_0)}$ eq.17

Where:

- $Q_{Gasification}$ = gasification heat requirement
- Q_{HRSG} = heat recovery steam generator heat
- $W_{gasfication}$ = gasification work input/requirements
- W_{GT} = gas turbine work output
- W_{HRSG} = Heat recovery steam generator work output
- W_{net} = overall process work output
- T_H = gasification temperature
- T_o = ambient temperature
- $T_{compresion}$ = compressor exit temperature
- $T_{combustion}$ = turbine combustion temperature
- $T_{turbexit}$ = turbine exit temperature
- T_{HRSG} = steam temperature

- P_{Ratio} = turbine pressure ratio
- η_{work} = work efficiency
- $\eta_{thermal}$ = thermal effeciency
- C_P = heat capacity at constant pressure
- γ = compression factor

6.3.2.1 Effect of compression ratio

Figure 6.5 presents the net-work output (eq. 11 or stream $W_{gasturbine}$) and net-work efficiency (eq.14) as a function of compression ratio. As expected, higher pressures lead to greater turbine workout put and net-work efficiency. However, at higher pressures, the gas turbine workout tends to flatten. To reach 70% work efficiency, the compression ratio in the turbine should be 1400 and combustion temperature should be 3375 °C. This is not possible with the current technology. The current technology for coal and natural IGCC gas turbines used can only accommodate an inlet gas temperature of 1200-1700 °C. considering a process that allows an inlet gas turbine temperature of 1600 °C, a turbine compression pressure of 100 bar achieves a work and thermal efficiency of 63.7% and 62.3%.

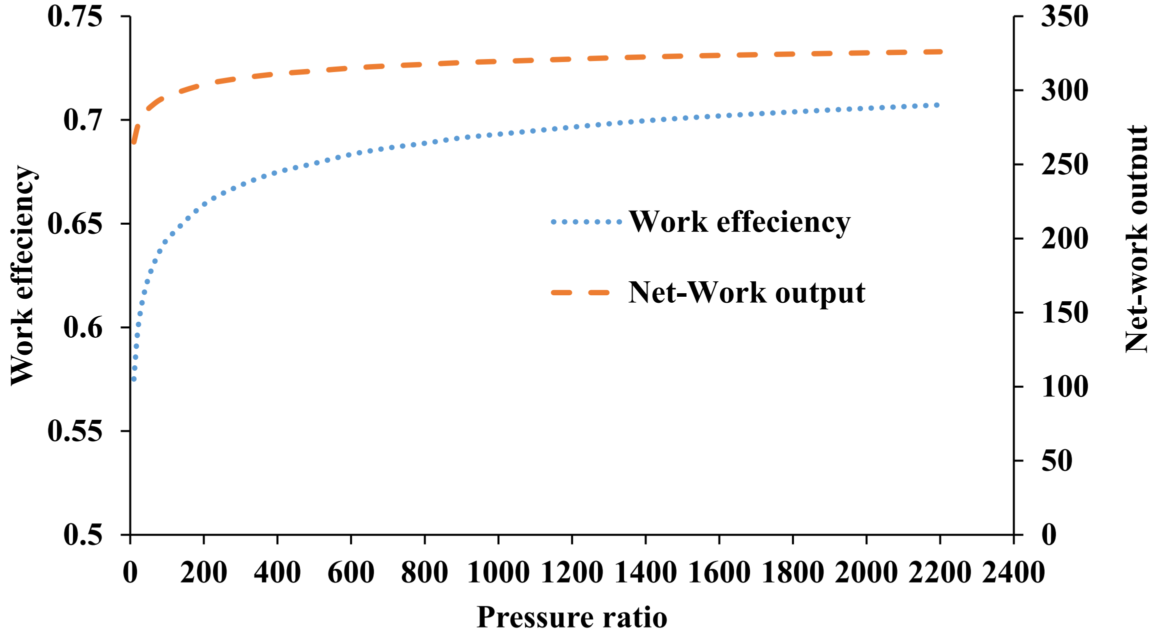

Figure 6.5. Gas Turbine work-output as a function of pressure ratio.

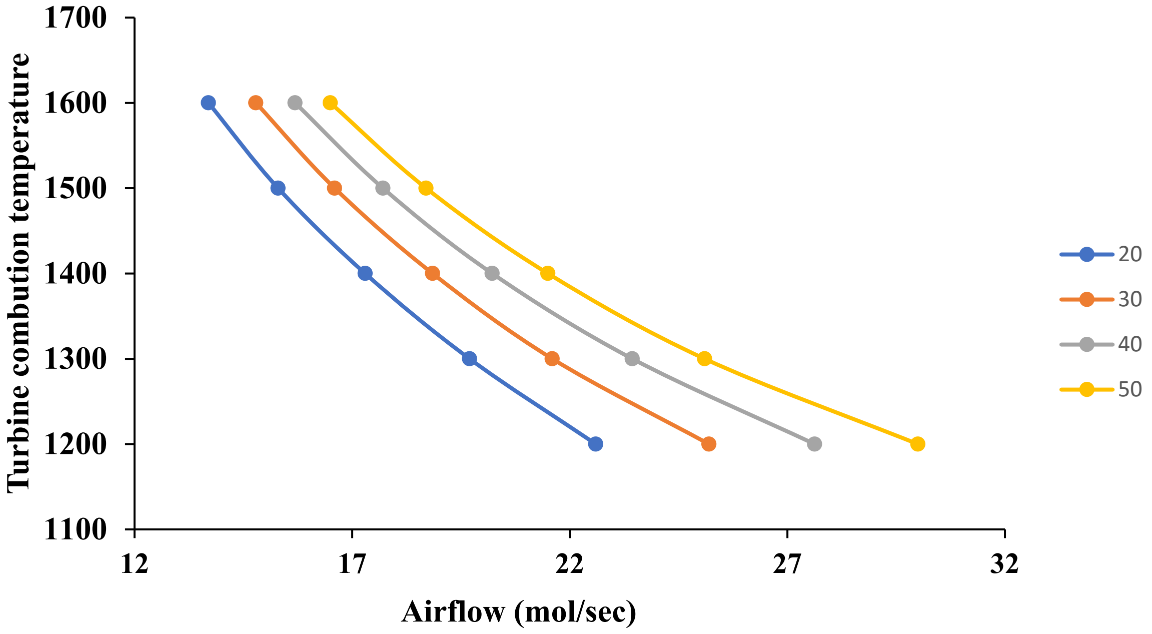

Figure 6.6. Effect of airflow rate on the combustor temperature.

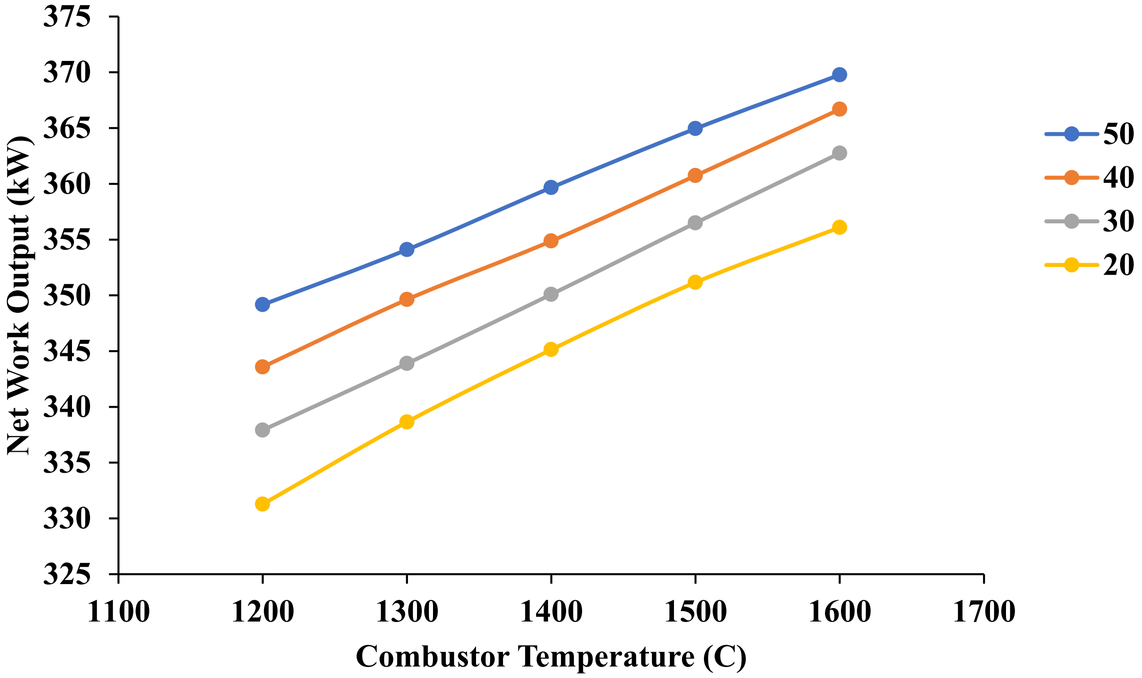

Figure 6.7. System work output as a function of combustor temperature.

6.3.2.2 Effect of airflow

The airflow is used to control the combustor temperature of the gas turbine, and Figure 6.6 shows the effect of airflow on temperature. Low airflow rates and high pressures result in higher combustion temperatures. The higher the airflow rates, the lower the combustion temperature and the less efficient the gas turbine will become. Therefore, the efficiency of the turbine decreases with an increase in the airflow rate. Figure 6.7 shows that the higher the combustion temperature of a turbine, the greater the work output and the more efficient the overall system becomes. Diminishing returns can be observed in Figure 6.7. Increasing the pressure ratio from 20 to 30 has a bigger gain than increasing from 40 to 50.

6.3.2.3 Exhaust temperature

Higher combustor temperatures result in higher exhaust gas temperatures, the thermal efficiency of the process significantly decreases as the exhaust temperature increases. Higher sulphur fuels exhaust temperature is often around 150 °C. A system utilising a turbine with a combustor temperature of 1600 °C and a compression ratio of 20, the efficiency would drop from 60.4% to 48.8% when the exhaust increases from 25 °C to 150 °C. At 50 bar compression ratio, the maximum thermal efficiency achievable would be 50.5% at the same conditions. Economisers are used to improving power plants efficiency by transferring the heat from the hot exhaust gas to the feed water going into the boiler. This means less heat is lost to the environment.

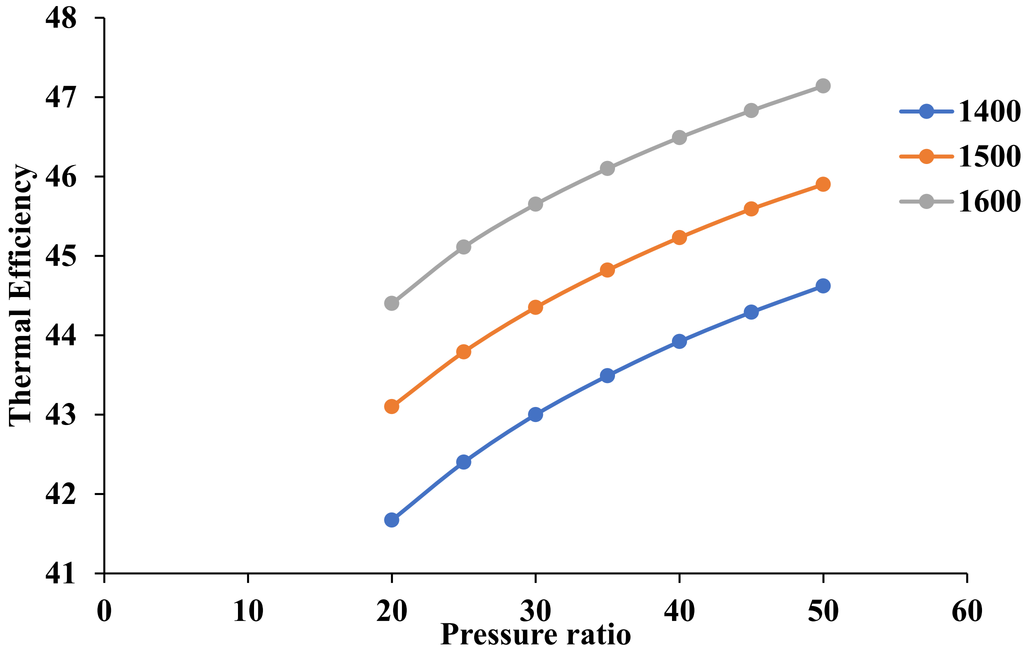

Figure 6.8. Thermal efficiency as a function of pressure ratio and turbine.

6.3.3 Design of 518ton/day waste tire IGCC system

Previous analysis showed that with the IGCC technology, it is possible to convert the chemical potential of tires to power. However, excessive operating pressures and temperature are required to achieve these high efficiencies. Current commercial gas turbine technology can only achieve a maximum work and thermal efficiency of 63% as supposed to the 96.7% discussion in section 1.

This section now assesses waste tires as a possible feedstock for an IGCC that is designed based on the annual waste tire rising in South Africa. The gasifier operating temperature and pressure are 1300 ºC and 24 bar. The tires are mixed with water to produce a slurry and fed to the gasifier at ambient conditions. In the previous analysis, the energy needs for gasification ignored the fact that the components must be raised to the gasification temperature. To design a process, the sensible heat to raise the products to the gasification temperature must be considered. The energy balance for the gasification unit is calculated using a variation of eq.4 as follows:

$$\Delta H_{gasification} = n_p \, \Delta H^o_{products} + n_p \int_{25}^{1300} \Delta C_p dT - n_r \, \Delta H^o_{reactants} \qquad \text{eq.18}$$

Since the liquid water is used instead of oxygen a subsequent amount of energy, 114.87 MW is required to drive the gasification step. This energy will be supplied by taking a fraction of the electricity produced by the system, utilising a basic heat pump, as shown in Figure 6.4. With the use of equations 8-17, the maximum achievable thermal efficiency as a function of pressure ratio and turbine combustion temperature was determined and shown in Figure 6.8. In Figure 6.8, the thermal efficiency increases by approximately 2.5% when the combustion temperature is increased from 1400 ºC to 1600 ºC, and the pressure ratio is fixed. Whereas, the overall net-work output improves by 5 MW when the temperature is increased. the same is observed when the pressure is increased. When the pressure ratio is increased to 50, the thermal efficiency increases by approximately 2.7%. However, the difference in efficiency decreases as the pressure increases such that at pressures above 50 bar, the efficiency increase is less than 0.3%. since larger compression ratios require expensive equipment, for a waste tire IGCC, one can sacrifice efficiency for an overall cheaper system to make the investment sustainable.

Hence, a waste tire IGCC with a gas turbine operating at 30 bar pressure ratio and 1600 ºC combustion temperature is selected. This system will produce a net-work output of 89 MW at a thermal efficiency of 45.65 % and or work potential efficiency of 45% when the exhaust temperature is set 25 ºC. Table 6.2 shows the parameters for the process envisaged by this work. Such a process would be self-sustainable and generate power that can contribute to the countries strain the electrical grid.

Table 6.2. Proposed process parameters.

$T_{gasification}$	1300	ºC
$W_{gasification}$	114.79	MW
Water flowrate	7.76	kg/s
Tire flowrate	5.9	kg/s
$T_{combution}$	1600	ºC
P_{ratio}	30	
$T_{exhaust}$	25	ºC
Turbine Air flowrate	182.16	kg/s
W_{GT}	148.95	MW
W_{HRSG}	35.12	MW
W_{net}	**89**	MW
Work efficiency	44.97	%
Thermal efficiency	45.65	%

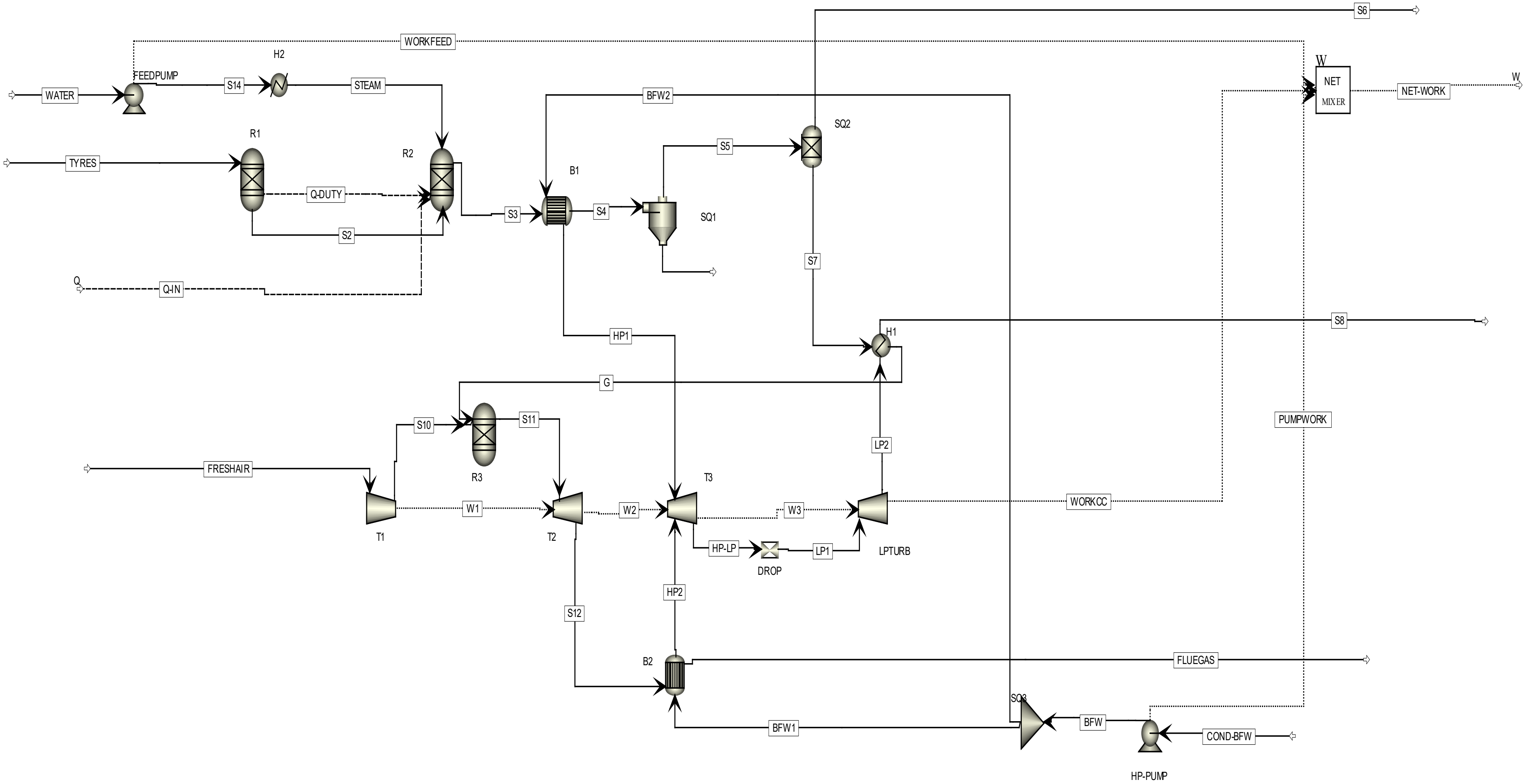

Figure 6.9. Aspen Plus Waste tire IGCC.

Table 6.3. Generated power using Aspen Plus.

Steam turbine	32.92	MW
Gas turbine and compressor	148.08	MW
Power consumption		
BFW pumps	0.7	MW
Feed pump	0.041	MW
Boiler	22.59	MW
Gasifier	94.89	MW
Net power	62.75	MW
Thermal input (LHV of tires)	196	MW
Overall efficiency	32	%

Figure 6.9 shows the process developed in Aspen Plus to meet the above targets identified in Table 6.3. Aspen Plus is chosen because it can incorporate all the vast reactions involved gasification and combustion and all the physical characteristics of the reactors. The ideal equation of state is selected to estimate all physical properties for all conventional components and unit operations in the process. Waste tires and ash are defined as non-conventional components, and the HCOALGEN and DCOALGT models are selected to estimate the enthalpy and density of non-conventional conventional components. The ultimate and proximate analysis are presented in Table 6.1.

The process takes in a 44.77% w/w slurry and produces a net-work output of 62.75 MW, at a thermal efficiency of around 32%. Table 6.3 describes the overall performance for the Aspen Plus flowsheet. The results from Aspen simulation are smaller than the value predicted using thermodynamic analysis. The discrepancy is because the lowest achievable exhaust temperature Aspen Plus® was 106 ºC whereas, with the thermodynamic calculations, the exhaust temperature was set at 25 ºC. However, despite this discrepancy, the energy being produced by the IGCC system is distinctly higher than the energy needed by gasification. The system is thus sustainable and generates excess electrical power for distribution. A renewable source such as solar or biomass mass can be used to supply the energy needed by gasification to avoid diverting the power from the IGCC system to be utilised. Another method to reduce the energy requirements of the gasifier is to burn a fraction of the feed with oxygen and vaporised the feed water to the gasifier. Conventional coal IGCC with oxygen feed generates about 9.6 GJ/ton. The developed waste tire IGCC process produces 10.52 GJ per ton of tires; however, no oxygen feed and steam generation. This means less investment in air separation units. The positive results suggest that waste to energy processes should form part of the integrated waste tire management solution and could be by far the most practical and environmentally safe option for waste tires.

6.4 Conclusion

Waste tire to power plants has been analysed using fundamental thermodynamics. The IGCC system has been shown as the process capable of conserving the chemical potential of waste tires. A slurry fed IGCC system which does not use oxygen or air during gasification was therefore considered as the potential process to utilise the waste resource. A sensitivity analysis of major operating parameters on the process was studied. The result of the thermodynamic analysis showed that a system with net-work output of 89 MW and a thermal efficiency of 45.65% is achievable. These results correspond to a gasification temperature of 1300 °C, a gas turbine combustor temperature of 1600 °C, and a 30bar pressure ratio. The feed to the process is a slurry feed with a solid concentration of 44.77wt%. Aspen plus was used to validate the calculated results. However, the results from Aspen Plus were significantly less than the predicted with an overall net efficiency of 32%. Despite the discrepancy waste tire IGCC net-work output was found to be 10.5 GJ/ton of tire much higher than that of conventional coal IGCC at 9.6 GJ/ton of coal. The waste tire IGCC developed is better than the conventional method in that it does not use oxygen for gasification, thus saves on capital cost required for air separation and waste tires can be delivered for free by the government. Above all, this work seeks to show that power generation should be considered as the practical route for waste tire management in South Africa.

Acknowledgments

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7 Methanol and power production from waste tires: a process synthesis approach

Publish research article

Title: **Methanol and power production from waste tires: a process synthesis approach**

Book series: Computer-Aided Process Engineering

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Short summary

So far, we have shown that waste tires can be converted into synthetic fuels through gasification and pyrolysis as well as electricity via the integrated gasification combined cycle (IGCC). However, these processes were evaluated independently. In Chapter 3, the thermodynamic analysis showed that 45% of the carbon resource is lost to carbon dioxide when tires are converted to liquid fuels, wax, and combustible gas. Whereas in Chapter 6, when tires are converted to electricity, the achievable thermal efficiency is 45.65 % using currently available technology but also all the carbon resource is lost to carbon dioxide. However, the two processes can be combined into a polygeneration process that can improve performance and reduce the loss of carbon resources. In this chapter, combined chemicals and power production from waste tires are thus explored using process synthesis. In particular, we determine the limit of performance for the co-production of methanol and electricity from a fundamental thermodynamic perspective. There are two primary advantages of a polygeneration system. First, efficiency increases when multiple processes are integrated together into one chemical system that is able to take advantage of synergies between them (for example, the heat released from one process can be used to drive another that requires heat). Second, the revenue potential is higher when more than one product is produced, and the system can be operated in a flexible manner such that the proportions of products produced are in response to fluctuating market prices. For the system developed here a carbon efficiency of 54.6% and the chemical potential efficiency of 63% were achieved. Equally, the system produced 2.42 GJ/ ton of waste tire and has the potential to generate a revenue of $ 620/ton of waste tire. The study shows converting tires to electricity and methanol is achievable, however, 45% of the carbon resource will end up as carbon dioxide.

Declaration by canditate:

The scope of my contribution to the chapter is as follows:

Planning simulation	100%
Conducting the simulation	80%
Results interpretation	80%
Compilation of the chapter	100%

The following co-authors have contributed to this chapter as per following:

Co-author	Nature of contribution		Contact and signature
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	Revision of chapter	50%	
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	Revision of chapter	50%	
Ephriam Llane	Conducting the simulation	10%	Email: llanemaphala@gmail.com

I declare that the above information is true and reflects the nature and extent of the contributions of the candidate and the co-authors

Signature of candidate:……………………..

Date:…………………….

Methanol and power production from waste tires: a process synthesis approach

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Abstract

Waste tires are part of solid waste materials that are toxic to the environment but have the potential to be converted into something of value. South Africa contributes approximately 11 million tires to the global 1.5 billion tires produced per annum. With waste tires identified as a potential energy source due to their high carbon content and heat value, it is not surprising that the government of South Africa has invested in the creation of a waste tire management plan intending to recover products and energy from this waste material. In this paper, a waste tire to methanol and electricity process is assessed from a thermodynamic and environmental perspective. Two key factors are analyzed, carbon efficiency and chemical potential efficiency. The purpose of this study is to contribute to this research by finding the limit of performance for the conversion of waste tires to methanol and power from a fundamental thermodynamic perspective. For the system developed a carbon efficiency of 54.6% and the chemical potential efficiency of 63% were achieved. Equally, the system produces 2.42 GJ/ ton of waste tire and has the potential to generate a revenue of $ 620/ton of waste tire. The study shows converting tires to methanol is achievable, however, 45% of the carbon resource will end up as carbon dioxide.

Keywords: gasification, waste-to-methanol, electricity, carbon emissions, efficiency

7.1 Introduction

Solid waste materials such as biomass, waste tires, and municipal solid waste, have been shown to contain adequate energy content to have the potential to substitute fossil fuels in the production of power and useful chemicals. Many existing technologies currently used for solid fossil fuels can be utilized easily to accommodate these waste materials, thus making the transition to alternate fuels achievable. Much of research in energy has largely focused on the optimization of technologies such as gasification, pyrolysis, combustion, and liquefication to estimate the optimum operating conditions to efficiently convert solid waste materials to useful products and power.

Developing countries such as South Africa have seen an increase in energy needs as the economy grows to include the participation of previously disadvantaged persons [1]. However, South Africa's energy needs have been in dire straits in the last decade with the state producer Eskom losing most of its available capacity plunging the country into stage six load shedding [2]. Equally, the country saw the cost of liquid fuels also increasing due to the weakening currency and fluctuations in global crude oil prices, and demand. In response, the government announced a plan to invest in alternative energy systems such as solar, wind, and waste-to-energy processes [3]. In terms of waste generation, the country has identified 38 waste streams that need to be diverted from landfills, and one such waste material is waste tires. South Africa contributes approximately 11 million tires to the global 1.5 billion tires produced per annum. With waste tires identified as a potential energy source due to its high carbon content and heat value, it is not surprising that the government invested in the creation of a waste tire management plan intending to recover products and energy from this waste material [4].

Various studies have shown that the conversion of waste tires through gasification technology is the best choice to utilize this hazardous waste material [5]. Gasification allows for the tires to be converted to syngas, an intermediate product to the production of high-value energy chemicals. Subramanian et al [6] investigated the thermodynamic, economic and environmental performance of waste tire to liquefied synthetic natural gas (methane) concept from a systems analysis perspective. The thermodynamic analysis result shows that 0.37 kg of liquefied methane is obtained for each kg of waste tire gasified. The overall energy efficiency of 43.6% was achieved for a system with no carbon capture system and 39% with a pre- and post-combustion carbon capture system. However, the economic analysis suggests that the selling price for the obtained liquified methane is not competitive with the natural gas selling price, coming in at six times the natural gas selling price. Rivarolo [7], investigated the feasibility to produce methanol via CO_2 hydrogenation using different renewable sources such as biogas, wind, and solar. Their results suggested that using biogas as feed gives the best economic performance. Borgogna [8], used Aspen plus to investigate the main parameters affecting the syngas quality, overall process yield, and emissions when municipal solid waste is converted to methanol via gasification. Their result shows that there is an environmental benefit to converting waste into methanol than burning it for energy as the CO_2 emissions are reduced by an average of 14%. Whereas [9,10] studies show that converting refuse-derived fuel to methanol leads to about 40% and 30-35% reduction in greenhouse gas emissions for methanol production from fossil fuels and bio-resources, respectively and waste to methanol process CO_2 emissions are half the emissions produced by waste to energy route. Biernacki [11] showed that it is possible to convert the whole CO_2 available from wastewater treatment plant via available excess electricity, to renewable methanol for chemical industries. Studies by [12,13] reveal the potential of the co-production of methanol and electricity from coal via IGCC plants.

The purpose of this study is to contribute to this research by finding the limit of performance for the conversion of waste tires to methanol and power from a fundamental thermodynamic perspective.

7.2 Methodology

In this work, the thermodynamic efficiency of the process converting waste tire to methanol and power is measured using two basic metrics, mainly: carbon efficiency and chemical potential efficiency. The properties are described as follows:

$$Carbon\ Efficiency\ (C_{eff}) = \frac{moles\ of\ C\ in\ the\ desired\ product}{moles\ of\ C\ in\ the\ feed} \quad (1)$$

$$Chemical\ Potential\ Efficiency\ (\eta_{cp,eff}) = \frac{Gibbs\ free\ energy\ of\ combustion\ of\ products}{Gibbs\ free\ energy\ of\ combustion\ of\ feed} \quad (2)$$

Equation 1 measures how much of the carbon in the feed stream ends up in the desired products. Less than 100% carbon conversion leads to carbon dioxide emissions. Equation 2 measures how much of the chemical potential stored in the feed material is translated to the desired products during chemical transformation. The concept of chemical potential efficiency target was first introduced in [14] where it is shown that the chemical potential efficiency can be translated into work or useful energy conservation. The thermodynamic properties of waste tires utilized in this work can be found in [15].

7.3 Results and Discussion

7.3.1 Methanol production from tires

The process involves the gasification of tires to syngas and then converting the syngas to methanol. Figure 7.1 shows a block diagram of the system producing methanol. The process starts with the gasification of tires with steam to produce syngas. Steam is selected as the gasification agent since it yields a higher composition of H_2/CO compared to oxygen. Through gasification, the produced syngas can be cleaned of toxic gases providing environmentally friendly beneficiation of waste tires.

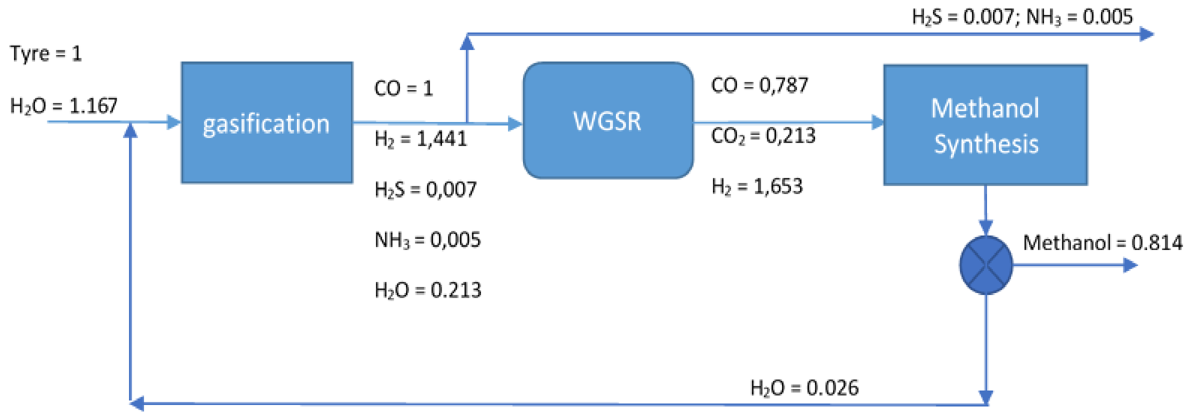

Figure 7.1. The methanol-producing process from waste tires.

The material balance for syngas generation using steam is:

$$CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 0.98H_2O = CO + 1.44H_2 + 0,007H_2S + 0,005NH_3 \quad (3)$$

$$\Delta H = 185.85\ kJ, \qquad \Delta G = 134.21\ kJ$$

It is assumed that all the available sulfur leaves as hydrogen sulfide, since chemicals in the tire rubber, such as zinc oxides, prevent sulfur-oxidizing.

The syngas from gasification is cleaned of acid gases and its H2/CO ratio is adjusted in the water gas shift reactor to meet the required ratio for methanol in the synthesis reactor. The recommended ratio of H2/CO is 2. The material balance needed to maintain this ratio is:

$$1CO + 1.44H_2 + 0.213H_2O = 0.213CO_2 + 1.653H_2 + 0.787CO \quad (4)$$

$$\Delta H = -8.75\ kJ, \qquad \Delta G = -6.07\ kJ$$

The adjusted syngas is fed to the methanol synthesis reactor and the mass balance in the reactor is (assuming complete conversion of CO):

$$0.787CO + 1.653H_2 + 0.213CO_2 = 0.814CH_4O + 0.186CO_2 + 0.026H_2O \quad (5)$$

$$\Delta H = -103.11\ kJ, \qquad \Delta G = -23.16\ kJ$$

The overall material for the process of producing methanol.:

$$CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 1.166H_2O = 0.814CH_3OH + 0.186CO_2 + 0.007\ H_2S + 0.005\ NH_3 \quad (G1)$$

$$\Delta H = 73.99\ kJ, \qquad \Delta G = 105.36\ kJ$$

The performance of this process in figure 1 is as follows:

$$Carbon\ efficiency = 81.4\%$$

$$\eta_{cp} = 86.3\%$$

Figure 7.1 and equation (G1) represent the ideal process or the maximum achievable conversion of waste tires to methanol. This process represents a case where all the units are energy integrated, with all the units that are exothermic sending their energies to the endothermic gasification step. That is, the water-gas shift, and the methanol synthesis will send all their energy to the gasification step, to try and achieve an adiabatic process. However, the overall mass balance of the process shows that the system still requires energy input. If this energy is not added the process would thus be infeasible. An additional amount of feed (tires) can be burned to supply the needed energy. Since the Gibbs free energy is greater than the enthalpy, it means that this process cannot be adiabatic but can achieve a work neutral. Since the target is work neutral the process will produce excess heat. Figure 7.2 shows the system that is fully integrated and the overall material balance for the system is:

$$1.231CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 1.057H_2O + 0.284O_2 = 0.814CH_3OH + 0.418CO_2 + 0.009\,H_2S + 0.006\,NH_3 \qquad \text{(G2)}$$

$$\Delta H = -29.9\,kJ, \qquad \Delta G = 0\,kJ$$

The performance of this process in Figure 7.2 is as follows:

$$Carbon\ efficiency = 66\%$$

$$\eta_{cp} = 70.1\%$$

Therefore, supplying the required energy by burning an additional amount of tires increases the carbon emissions by 44% and the chemical potential efficiency decreases from 86% to 70%. The process can be reversible if the excess heat can be recovered from the process in a way that doesn't put additional work. However, it must be said that the gasification step operates at higher temperatures than the other steps, this essentially means that the energy would have to move against a temperature gradient and practically that might require expensive equipment. Therefore, full integration may not be possible with conventional technology.

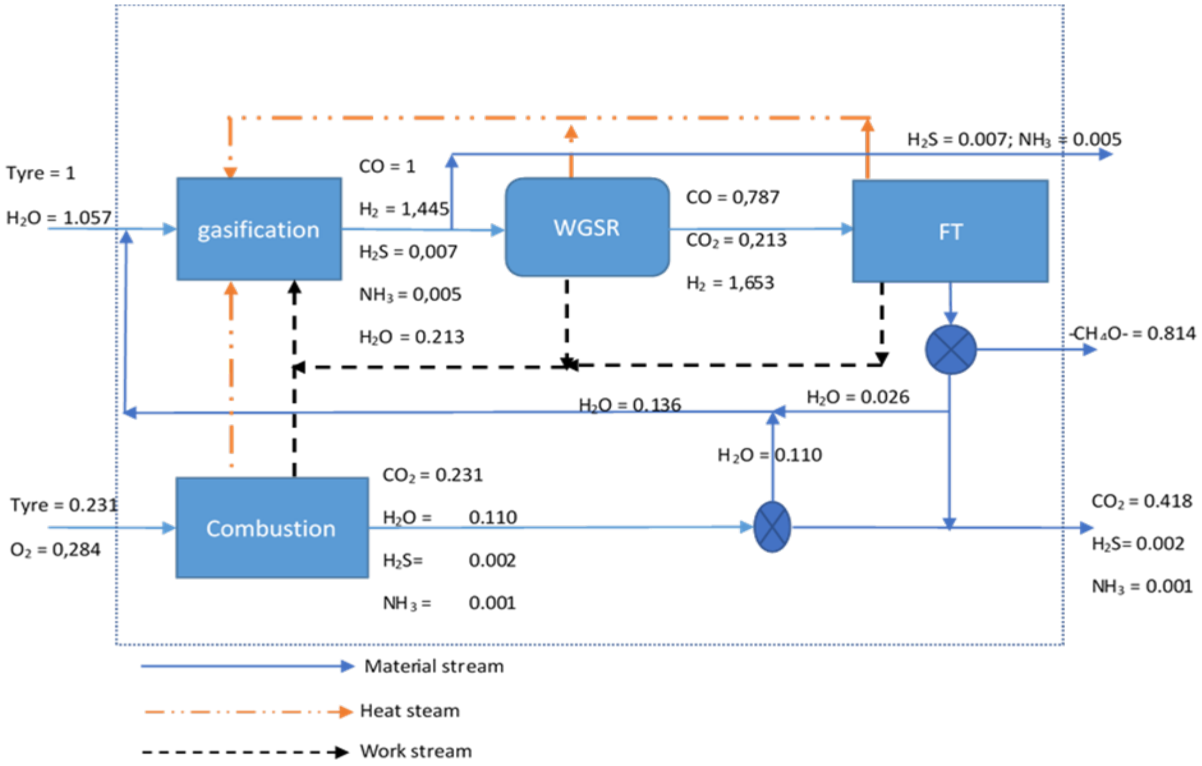

Figure 7.2. Fully integrated methanol process.

The second option to supply the energy required by the process in Figure 7.1 is to burn an additional amount of feed to supply the gasification step and leave the other two units unintegrated. The material balance for the combustion of tires to make the gasification step adiabatic (partial integration) is:

$$0.413CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 0.506O_2 = 0.196H_2O + 0.413CO_2 + 0.003\,H_2S + 0.0021\,NH_3$$

$$\Delta H = -185.85\,kJ, \qquad \Delta G = -188.54\,kJ$$

Figure 7.3 and equation G3 shows the overall material balance to produce methanol when additional tires are burned to supply the energy needed for the gasification step only.

$$1.413CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 0.971H_2O + 0.506O_2$$
$$= 0.814CH_3OH + 0.599CO_2 + 0.010\,H_2S + 0.0071\,NH_3 \qquad \text{(G3)}$$

$$\Delta H = -111.23\,kJ, \qquad \Delta G = -82.55\,kJ$$

The performance of this process in figure 3 is as follows:

$$Carbon\ efficiency = 57.6\%$$

$$\eta_{cp} = 70\%$$

The system described by Figure 7.3 and equation G3 shows the overall process will release energy. If not recovered the system won't achieve reversibility. The more efficient the system is the closer it recovers the excess energy. Applying heat engine at the different units, work will be recovered through the released heat in these units. however, when applying the notion of heat engines to chemical processes, heat can only be used to satisfy work requirements at a single temperature, the Carnot Temperature. Therefore, if the heat engines utilise steam, that steam must be generated at the Carnot temperature of the units. Also not fully intergrading the process means more tires must be burned and this increases the carbon dioxide emissions and thus the carbon efficiency of the process reduces to 57%. However, the process also produces 82.55 kW of shaft work which can be converted to electricity. Considering the production of electricity maintains the chemical potential efficiency of the process at 70%.

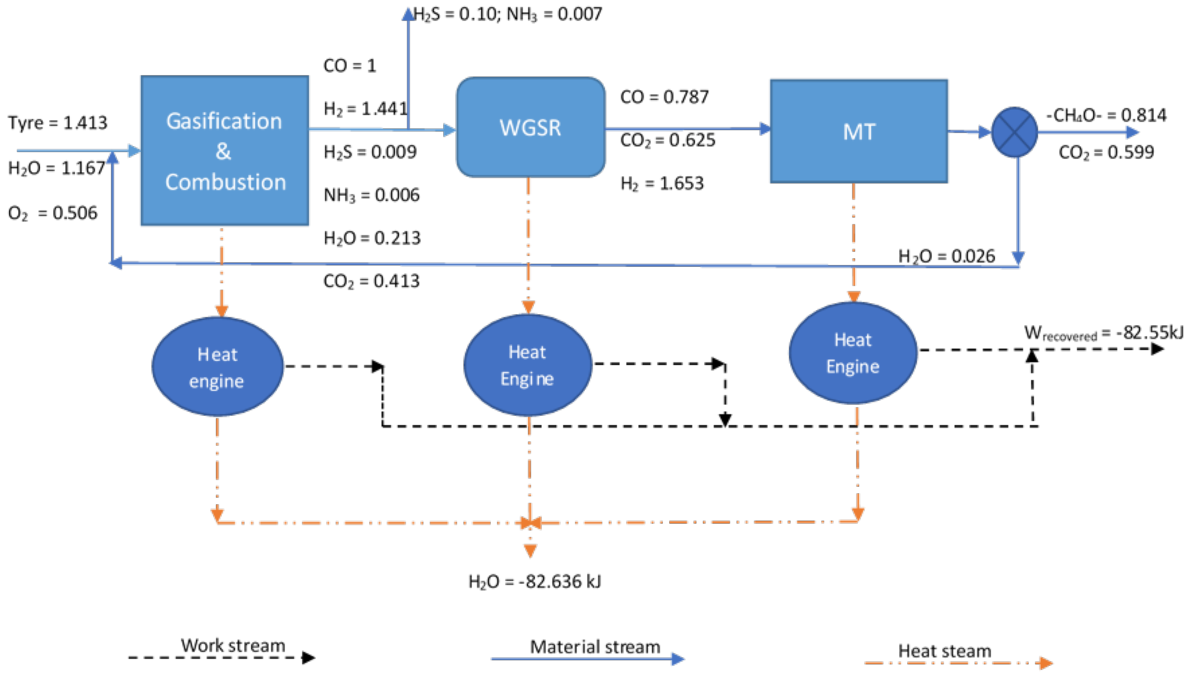

Figure 7.3. Partially integrated methanol process.

7.3.2 Effect of temperature

Due to kinetic limitations, all units need to operate at a temperature than Carnot temperature. The gasification must operate at temperatures above 1000ºC to ensure complete conversion of the carbon sources whereas the water gas shift and methanol synthesis reactor must operate at temperatures befitting the catalyst used. 1300ºC is recommended for gasification of waste tires 450ºC for water gas shift and 220ºC for the methanol synthesis. Operating at a temperature other than the Carnot temperature result in the loss of some of the potential work. To compensate for the lost work, more feed is burned and however, this increases the CO_2 emissions. The operating temperature for the water gas shift reactor is greater than the Carnot temperature, which means the unit will require further work input since operating at higher temperatures than Carnot temperature recovers more work than the system can provide. Using the notion of heat engines, the work produced by the process reduces from 82kW to 48 kW, which is equivalent to 2.42 GJ/ ton of waste tire. An additional amount of 0.492 mol/s of tires is required to make the process feasible. Figure 7.4 shows the process diagram for a system operating at temperatures than Carnot. For the system described by Figure 7.4 the carbon efficiency decreases to 54.6% and the chemical potential efficiency decreases to 63%. This, therefore, means that converting tires to methanol is achievable, however, 45% of the carbon resource will end up as carbon dioxide. Furthermore, by operating the gasification unit at elevated pressures and then expanding the gaseous products, extra work will be recovered.

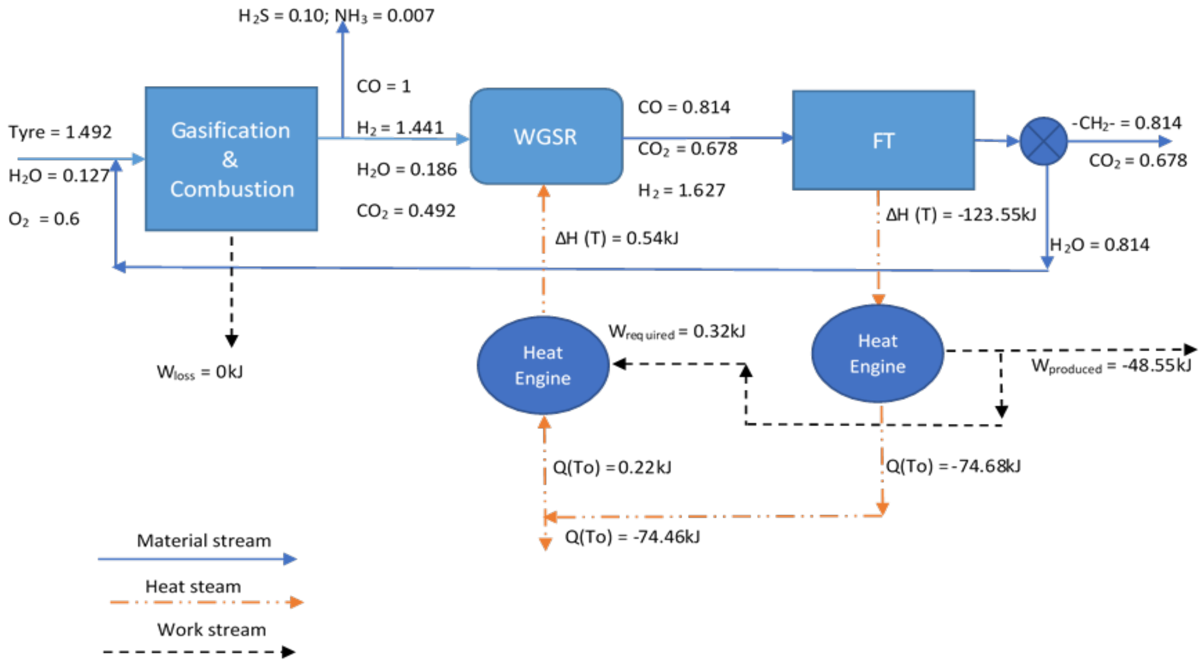

Figure 7.4: Methanol process operating at lower than Carnot temperatures.

7.3.3 Revenue potential

The revenue potential of the process is obtained by a difference of the product selling price and of the cost of feed material. The analysis excludes the capital costs associated with each pathway. When electricity is sold at \$ 0.098/kWh and methanol sold at \$ 480/ton (Global petrol prices," 2019), the process in Figure 7.4 has the potential to generate a revenue of \$ 620/ton of the tire.

7.4 Conclusion

This work presented a method for process analysis at the "systems" level. This method allows a "big picture" perspective. Such an elevated perspective further allows for the possibilities and limits to be investigated before significant time and resources are expended in more details-orientated methods. The analysis presented here focused on the performance limits of converting waste tires to methanol and power. A notable result of this method shows that high process efficiency can only be achieved through a high degree of process integration and with the practice of co-production. Highly specialized processes that focus on producing only a few products, will always make a sacrifice in overall process efficiency. This study showed that 45% of the carbon feed is lost to carbon dioxide when tires are converted to methanol and power. However, the process has a revenue of approximately \$ 620/ton of waste processed. Therefore, from an economic perspective, converting waste tires to methanol is preferable to landfilling, as it reduces the volume of a hazardous waste stream by converting it to a useful transportation fuel and power. However, another pollutant, CO_2 is produced.

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8 Methanol synthesis and hematite reduction using waste tires

Publish research article

Title: **Methanol Synthesis and hematite reduction using waste tires**

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Short summary

We have discussed in the previous chapter, that polygeneration processes can be advantageous in terms of profitability and efficiency. Chemical production processes can be synergistically integrated with power generation systems to overcome the high energy consumption required in chemical production plants. The operation of polygeneration systems can also be varied such that it follows market trends. In this chapter, we consider the use of waste tires in the process of iron making, as well as the possibility of integrating methanol synthesis into the process of iron making. Process synthesis methods are used to analyze and determine the fundamental thermodynamic limitations of such a process and to gauge its commercial potential through process performance targeting. Coal is the primary source of fuel used in iron making. The iron and steelmaking process can be broken down into five major process operations: sinter production, coke production, iron production, iron preparation, and steel production. Iron production is the heart of it all, and it is the most energy-intensive process. Solid feed materials such as iron ore pellets, limestone, and coke are fed at the top of the furnace, whilst the hot air is blown into the furnace through nozzles at the bottom of the furnace. This facilitates the exothermic combustion of coke and the gasification of coal into heat and reduces gases (CO and H_2) required for the reduction of iron ore. Since the process produces syngas for iron ore reduction, excess amounts of CO, and H_2 can be withdrawn from the process. This syngas can be further used to produce other chemicals such as methanol, DME, olefins, and liquid fuels. However, drawing excess syngas from the process would increase the fuel requirements. It is for this reason that we consider the use of tires. South Africa for example generates 250 000 tons of waste tires per annum whilst over 900 000 tons remain in storage depots without a reuse plan. Since tires contain a thermal input energy similar to coal, iron-making seems a perfect process to utilize this wasted carbon resource. The aim of this study is to develop a preliminary combined methanol synthesis and ironmaking process using process synthesis tools. In this paper, we will identify the performance targets for processes of this type and develop a theoretical framework for their design.

Declaration by canditate:

The scope of my contribution to the chapter is as follows:

Planning simulation	100%
Conducting the simulation	100%
Results interpretation	80%
Compilation of the chapter	100%

The following co-authors have contributed to this chapter as per following:

Co-author	Nature of contribution		Contact and signature
Celestin B Sempuga	Results interpretation	20%	Email: Sempubc@unisa.ac.za Signature:
	Revision of chapter	100%	

I declare that the above information is true and reflects the nature and extent of the contributions of the candidate and the co-authors

Signature of candidate:……………………..

Date:…………………….

Methanol synthesis and hematite reduction using waste tires

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Abstract

Iron production and Steelmaking are very energy-intensive processes with an estimated global energy intensity of 16.5 GJ/ton. The whole process is dependent on natural resources for both energy needs and products. This results in global CO_2 emissions of 1.8 tons per ton of steel produced. It is however impossible to do away with the industry as it is the key component to our economy and existence. Therefore, key solutions are required to optimize this industry but maintain its output or production. This work proposes to supplant the coal used in steelmaking with waste tires to reduce operational costs. In this paper, process synthesis techniques are used to determine the fundamental thermodynamic limitations of such a process through process performance targeting. It is found that one ton of iron and 430 kg of methanol can be potentially produced from 1.42 tons of haematite and 479 kg of waste tires. However, 63% of the carbon resource will end up as carbon dioxide, equivalent to 985kg/ton of iron produced. This is still lower that the coal route which releases about 1.05 CO_2 tons/ ton of iron. This work provides a framework for designing and synthesizing waste tire reuse processes.

Keywords: Waste tires, Reduction, Methanol, Iron, Thermodynamics,

8.1 Introduction

The global energy needs are constantly increasing and as a result, the natural resources that sustain these energy demands are becoming scarcer and more expensive, whilst human-generated emissions and other solid waste are increasing to critical levels. All companies are now under pressure from societies to decarbonize or reduce emissions from their processes. One such process industry is iron ore reduction and steelmaking. Iron production and Steelmaking are very energy-intensive processes with an estimated global energy intensity of 16.5 GJ/ton [1]. The whole process is dependent on natural resources for both energy needs and products. This results in the global CO_2 emissions of 1.8 tons per ton of steel produced [2]. It is however impossible to do away with the industry as it is the key component to the world economy and existence. Therefore, key solutions are required to decarbonize this industry but maintain its output or production. The major contributor of carbon emissions from the industry is the use of coal. This work proposes to reduce the coal used in steelmaking with waste tires. Waste tires are derived from fossil fuels and currently at their end-of-life tires have no fundamental use and end up being dumped in landfills creating an unnecessary environmental problem. Waste tire generation in the developing worlds is one of the organic wastes that has not found a sustainable solution yet. For example in South Africa an estimated 250 000 tonnes of waste tires are produced each year adding to an existing stockpile excess of 900 000 tonnes spread across 26 national storage depots without a solid plan for reprocessing or recycling [3,4]. A draft waste tire management plan (IndWTMP) issued by the CSIR in 2022 indicates the combine recycle and reuse of waste tires is 20% while the rest are stockpiled. This is far in comparison to Europe where the recycling and reuse rate is excess of 95% [5,6]. The European Tire and Rubber Manufacturers' Association (ETRMA) reports that in 2019, Europe produced 3.26 million tonnes of waste tires and about 95% were collected and treated for material recycling and energy recovery. ETRMA statistics shows 48% of waste tires were treated through energy recovery and 52 % through material recycling. In South Africa 32% of the 54000 treated waste tires were utilised for energy recovery and 58% for material recovery [3]. Tires possesses a higher volatile content, higher heating value and a low ash content than coal and biomass [7]. If all waste tires produced in South African are converted to power up to 2GWh of electricity could be produced. Fossil fuels sustain South Africa's energy needs with only 2% coming from alternate sources. Successful use of waste tires for energy and power would improve the country's energy mix and alleviate some of the dependency on expensive fossil fuels such as diesel. Alternatively, waste tires can be used to produce a vast array of chemical products through thermochemical conversion processes such as gasification, pyrolysis, liquification, devulcanization.

This paper evaluates and determines theoretical performance targets for a combined methanol synthesis and iron ore reduction using waste tires as carbon source. The main constituents of tires are carbon and hydrogen and thus the reduction process simply involves reacting the carbon and hydrogen in waste tires with the oxygen in the iron ore to produce iron in its reduced form and carbon dioxide and water. However, in this work we explore co-production opportunities to improve the efficiency of the process by reducing CO_2 and H_2O production and thereby improve the material and energy efficiency of the process.

8.2 Methodology

We use a system approve to identify feasible process targets by first defining the attainable region of the process and systematically identify targets of interests subject to material and energy balances and thermodynamic constraints. The attainable region represents all possible product distribution from a given feed to a process. The work evaluates the thermodynamic efficiency of a combined iron ore reduction and methanol synthesis process using waste tires as carbon feed. The utilisation of raw materials, waste generation and the thermodynamic efficiency of the process will be assessed using the following four metrics [8].

$$Carbon\ Efficiency = \frac{moles\ of\ C\ in\ the\ desired\ product}{moles\ of\ C\ in\ the\ feed} \tag{1}$$

$$Atom\ Economy = \frac{mass\ of\ desired\ product}{Total\ mass\ of\ feed} \tag{2}$$

$$E - factor = \frac{Mass\ of\ waste\ produced}{Mass\ of\ desired\ product} \tag{3}$$

Equation 2 quantifies how much of the carbon in the feed stream ends up in the desired products. Any carbon that is not contained within a product will be lost in undesired by-products. Equation 3 provides useful information on the utilisation of all the feed and waste generation.

All analysis done here is based on one mole of waste tires input.

8.3 Results and discussion

Table 8.1 shows that waste tires have an LHV and carbon content comparable to coal, and thus have the potential to be utilized for a direct reduction of iron ore. As shown in Figure 8.1, one mole of tire, can reduce 0.542 mols of iron ore and produce 1.084 mols of Fe. The process is feasible with excess work, but all the carbon available in the feed is transferred to CO_2. Thus, the carbon efficiency of the process is zero. This corresponds to about 730 kg of CO_2 released to the environment per ton of iron produced during this process. When compared to coal, tires marginally perform better in terms of iron production and carbon dioxide emissions. Figure 8.2 shows for one mole of coal the iron production decreases by 5% and the carbon dioxide emissions increases to 763 kg CO_2 per ton of iron produced. The Atom efficiency as well the E-factor for waste tire process is 54% and 0.87 compared to coal which are 53% and 0.89, which indicates the ability of waste tires to replace coal. However, this is not a solution to carbon emissions if tires can only reduce emissions by 5%. An alternative route is required where the carbon emissions per ton of iron is reduced as an incentive to transition to waste tire feed process. The one way is to consider a co-production of methanol and iron using waste tires. In this way not all the carbon feed in the tire is used from reduction, but an indirect route is utilized where the tires are converted to syngas and syngas is used for the reduction and the excess syngas is used to produce methanol.

Table 8.1. Ultimate and proximate analysis [9].

Ultimate Analysis wt.%			**Proximate Analysis wt.%**			
	Tire	**Coal**		**Tire**	**Coal**	
C	85.05	67.69	Moisture	1.14	7.76	
H	6.79	4.59	Fixed Carbon	32.28	47.14	
N	0.5	1.13	Volatile Matter	62.24	34.05	
O	1.75	5.48	Ash	4.35	11.05	
S	1.53	2.3	LHV	34.9	30	MJ/kg

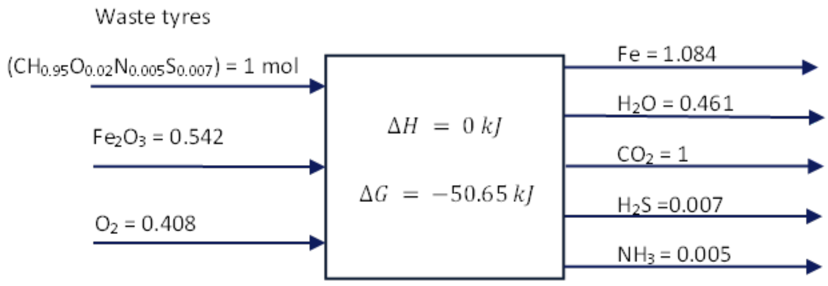

Figure 8.1. Reduction of iron ore with waste tires.

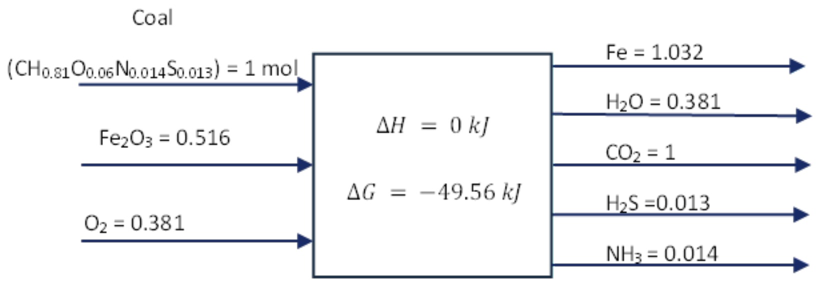

Figure 8.2: Reduction of iron ore with coal

For 100% raw material conversion efficiency and minimal impact on the environment, the law of conservation of mass implies that the elemental composition of the desired products must match that of the feed. Equation 5 shows the material balance for an integrated methanol synthesis and ironmaking process with 100% raw material conversion efficiency on tire feed. Tires contains a ratio of carbon to hydrogen close to one to one, therefore the eventual set of desired products (in combination), regardless of the process, must contain the same ratio of carbon to hydrogen, because any deviation would lead to the formation of unwanted products (i.e., CO_2), thus reducing the process material efficiency. The overall material balance for this process based on one mole of waste to produce methanol and iron ore from using waste tires for reduction is as follows:

$$CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 0.328Fe_2O_3 = 0.657\,Fe + 0.77CO + 0.23CH_4O + 0{,}007H_2S + 0{,}005NH_3 \tag{5}$$

$$\Delta H = 189.361\,kJ, \qquad \Delta G = 146.83\,kJ$$

Equation 5 shows that under ideal conditions one mole of tire feed can reduce 0.328 moles of iron ore to produce 0.657 moles of iron and 0.23 moles of methanol. However, in equation 5 we see that excess oxygen from iron ore leaves as CO and that the small ratio of hydrogen to carbon in the feed constrains the full conversion of Carbon to methanol. One can immediately see from the above equation that waste tires can never achieve the 2:1 ratio of hydrogen to carbon monoxide required for liquid fuel production. To achieve this ratio an additional amount of feed containing hydrogen often water is required, however often this additional feed comes in with an extra oxygen which must leave the system as carbon dioxide. equally, the system described in equation 5 requires energy input for it to be feasible as indicated by the positive ΔH and ΔG. A positive ΔG across a process indicates the amount of energy equivalent to mechanical work that must be supplied for the process to be feasible (we refer this as the work requirement of the process), while a positive ΔH indicates the total amount of energy to be supplied in the form of heat or work. Thus, additional oxygen can be fed to achieve a zero-energy requirement as shown in shown in eq.6.

$$CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 0.328Fe_2O_3 + 0.335O_2 = 0.657\,Fe + 0.101CO + 0.669CO_2 + 0.23CH_4O + 0.007H_2S + 0.005NH_3 \quad (6)$$

$$\Delta H = 0\,kJ, \qquad \Delta G = -25.219\,kJ$$

Therefore, supplying the required energy needed by the process in eq.5 by feeding more oxygen generates 0.669 mols of carbon dioxide thus reducing the carbon efficiency to just 33% and the chemical potential efficiency decreases from 86% to 70%. In the process described by eq.6, further optimization can be done to convert the excess CO to methanol through addition of water. The easiest route is to burn an additional number of tires and use water to increase the ratio of hydrogen to carbon. However, this approach also leads to increased CO_2 emissions. Thus, the overall material balance for a hypothetical full integrated and adiabatic process to produce methanol and iron is shown in eq.7 and Figure 8.3:

$$CH_{0.95}O_{0.02}N_{0.005}S_{0.007} + 0.252Fe_2O_3 + 0.285O_2 + 0.287H_2O = 0.504\,Fe + 0.627CO_2 + 0.373CH_4O + 0.007H_2S + 0.005NH_3 \quad (7)$$

$$\Delta H = 0\,kJ, \qquad \Delta G = -9.69\,kJ$$

$$Carbon\ Efficiency = 37.3\%$$

$$Atom\ Economy = 59\%$$

$$E - factor = 0.7$$

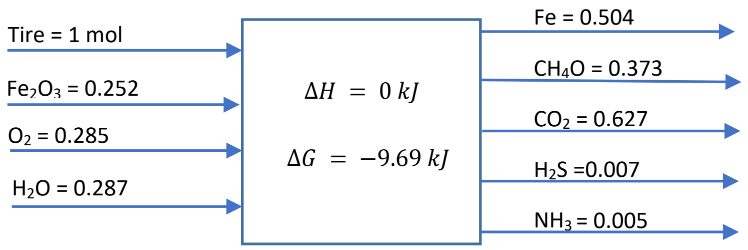

Figure 8.3: Process diagram for methanol and iron production from waste tires.

Eq. 7 shows that having additional amount of water enough to meet the ratio to achieve the hydrogen to carbon ratio of 2:1 increases the methanol production by 62%. The carbon efficiency is 37.3%. However, the amount of iron ore reduced decreases thus which decrease elemental iron production by 23%, and by 50% when comparing to the direct routes. This, therefore, means that combined iron ore reduction with methanol synthesis with waste tires as carbon feed is achievable. By equivalence, 1 ton of iron produced consumes 478 kg of waste tires and 1.42 tons of iron ore and 430 kg of methanol is co-produced. The production of methanol reduces the molar carbon capacity to reduce iron ore as such, the quantity of iron reduces by almost 50% this therefore means that per ton of iron the process produces 980 kg of CO_2. This is still lower than the coal route which is 1.05 ton per ton of iron. However, with pig iron currently priced at $ 1000 per ton, methanol at $ 370/ ton [10] and iron ore at $ 101.5 per ton [11], a high-level market-related revenue potential analysis of the different process pathways suggest the polygeneration of methanol and iron is most profitable. The revenue potential of each process pathway is obtained by a difference of price of selling products and of the cost of feed material. An estimated revenue of $1015 per ton of iron can be achieved for the polygeneration route compared to $855 per ton for the iron only route. But more capital investment is required for the poygeneration due to the different units required to achieve the required products.

8.4 Conclusion

The purpose of this article was to identify the most promising alternatives for waste tire utilization and present a conceptual target for the co-production of methanol and iron ore reduction. The assessment utilizes the carbon efficiency and Atom economy and E-factor. This assessment looks at how much of the carbon in the tire is used to produce useful products and how much of the feed content has been transferred to the products which indicates the potential impact to the environment. The results show that co-production with methanol reduces CO_2 emissions by 37.3% (from 1 mole CO_2 to 0.627 CO_2 for methanol case) and increases revenue by 15.6% (from 855 $ to 1015$).

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9 Techno-economic analysis of waste tires-to-chemicals and power plants: generation of methanol and Power

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Abstract

This work investigates the influence of tire levy on the minimum selling price of methanol and electricity produced from a polygeneration process utilizing waste tires as feedstock. Waste-to-energy and chemicals processes are often not cost competitive to fossil-based processes due to the high carbon taxes and often poor or lack of subsidies, and low thermal efficiency. However, since waste tires are an environmental hazard, waste tire conversion processes must be provided with competitive subsidies or levies to make them competitive with fossil-based fuels. In this study, two process models were developed to evaluate the potential to produce electricity and methanol from waste tires. In one process model, all the waste tire is used to produce electricity. In the second process model, methanol and electricity are produced. Aspen Plus and Aspen Hysys were used to simulating the detailed heat and material balance of the processes. The process modeling results, including the composition, flow rate, temperature, pressure, and enthalpy of different streams, were used to determine the sizes and cost of the process units and related equipment. A high-level economic model was prepared to evaluate the economic viability of the two processes.

9.1 Introduction

Waste tire generation and recycling are still a problem around the world. The USA alone generated over 274 million scrap tires representing over 5 million tons of scrap waste tires in 2021 [1]. Europe produced 4.24 million tons of tires in 2020 [2]. The amount of waste tires has also increased in developing countries. For example, in 2022 South Africa generated an estimated 250,000 metric tons of waste tires adding to an existing stockpile of 900,000 metric tons spread across 26 national storage depots without a robust plan for reprocessing or recycling [3,4]. The waste management bureau (WMB) of South Africa took over the responsibility of waste tire management in 2017 and has made collective efforts to divert waste tires from landfills into 28 depots across the country, where they wait for potential reuse. However, the WMB has been challenged with the development of processing capacity since it started managing waste tire operations. Many waste tires contracted processors stopped their operations in 2019 due to expired licenses, contract disputes, adherence to emissions standards, and non-profitability and others simply closed shop during post covid-19 lockdown. In South Africa, the recycling and reuse of waste tires are about 20% while the rest are stockpiled [3]. Whereas in Europe the recycling and reuse rate is more than 95% [5]. The European Tire and Rubber Manufacturers' Association (ETRMA) reports that by 2021, about 95% of waste tires were collected and treated for material recycling and energy recovery [2]. In the United States (US), over 95% of stockpiled tires have been cleaned up by 2021 and the recycling and reuse rate is more than 71% [1]. ETRMA statistics show 48% of waste tires were treated through energy recovery and 52 % through material recycling. However, the energy recovery route produces carbon dioxide and only contributes approximately 37% of the energy necessary to produce a new tire, however since other methods for waste tire material recycling have very limited industrial-scale implementation [6], thermal conversion is still the preferred option that offers more option in material and energy recovery. However, research and circular economy strategies related to the sustainable development of waste tire recycling technologies are still required to meet the rising production.

The WMB spends about R384 million each year for storage, waste pickers, and transport of waste tires to a dedicated site of storage and processing. A call through tender was issued in 2021 inviting all who can utilize the recycling and reuse of waste tires in a manner that does not harm the environment. The waste management agency will transport used tires to their gates (i.e. at no cost to the processor). In addition, the WMB will pay a predetermined processing charge of R0.31 per kilogram per tonne of processed waste tires to all certified waste tire processors. The National Waste Management Strategy (NWMS) identifies waste tire recycling as an area that may contribute to South Africa's economic growth and create green jobs [3].

This work presents a desktop economic study and optimization of a polygeneration process to produce electricity and methanol using waste tires as a carbon source. A techno-economic analysis is conducted to assess the required capital investment as well as the levy necessary to make these waste-to-energy processes cost-competitive to fossil-based plants. Polygeneration systems have an advantage in that multiple processes are integrated into one chemical system to take advantage of synergies between them thus increasing efficiency. For example, exothermic heat from one process drives an endothermic reaction in another. Second, profitability gains can be achieved by operating the plant flexibly enough to change the proportions of feedstocks used and the proportions of products produced in response to fluctuating market prices [7]. The costs have been estimated for a waste tire gasification plant in South Africa. The analysis is based on present-day conventional downdraft gasifier technology. Two cases are simulated, the one converts tire to electricity only, and the second produces methanol and power. For both cases, 550 tons/day of waste tires are fed, corresponding to about 216 MW thermal input. The performance of the developed process will be assessed against the performance targets set up in previously published work [8,9]. In prior work, we demonstrated through a high-level process synthesis that wastes tire gasification routes are better suited for waste tires than pyrolysis; however, there is a penalty of 45 percent carbon emissions and a high capital cost. Aspen Plus ® and Aspen Hysys ® are used in conjunction for the scale-up and optimization of the processes described in chapters 7 and 8. The impact of polygeneration, and tire tax, on economic performance, is determined using a sensitivity analysis.

9.2 Methodology

This work considers a polygeneration of methanol and power from waste tires through thermochemical conversion. The process discussed herein involves the gasification route. This involves the conversion of waste tires to syngas in gasification technology. This is followed by syngas cleaning and treatment to prepare it for methanol production. The syngas can also be combusted directly in gas turbines to generate electricity. The chemicals intended for study are methanol and power. A certain quality of syngas is required for each chemical and the syngas generated in the gasification step contains tar, particulates, sulfur gases, NO_x, and CO_2 and the H_2/CO ratio is less than 2. Therefore, a reforming step for tar, as well as water gas shift (WGS) is required during the preparation. Huge amounts of CO_2 are generated during the water-gas shift therefore CO_2 removal is also required.

Aspen Plus simulation software is utilized to develop three concepts of waste tire conversion. Mass and energy balances for most of the unit operations are developed using Aspen Plus

V12.1, except for the MDEA-based H_2S and CO_2 removal sections that are modelled using a simple separator, based on efficiencies published in the literature [10]. The performance of the processes is assessed using the thermodynamic analysis equations (1) and (2). Table 9.1 shows the thermal properties of waste tires used for the study.

Table *9.2* shows the configuration of processes.

Table 9.1. Thermal properties of waste tires.

	Ultimate Analysis wt.%						**Proximate Analysis wt.% (dry basis)**				
Ref.	C	H	N	O	S	Cl	Moisture	FC	VM	ASH	LHV
[11]	77.3	6.2	0.6	7.3	1.8	0	0	25.5	67.7	6.8	33.96

Table 9.2. Configuration of processes.

Configuration	**Description**
WT-P	The main product is electricity. All the syngas is sent to the combined cycle
WT-Methanol-P	Methanol is the main product, and all the off-gases are burned for electricity generation
WT-Methanol-E	Methanol is the main product; electricity is supplied for additional to all power-consuming units.

The Peng-Robinson equation of state with the Boston-Mathias modification (PR-BM) was used for physical property calculations for most units [12]. Figure 9.1 presents a flowsheet of the polygeneration concept that converts a waste tire feedstock to including methanol and electricity.

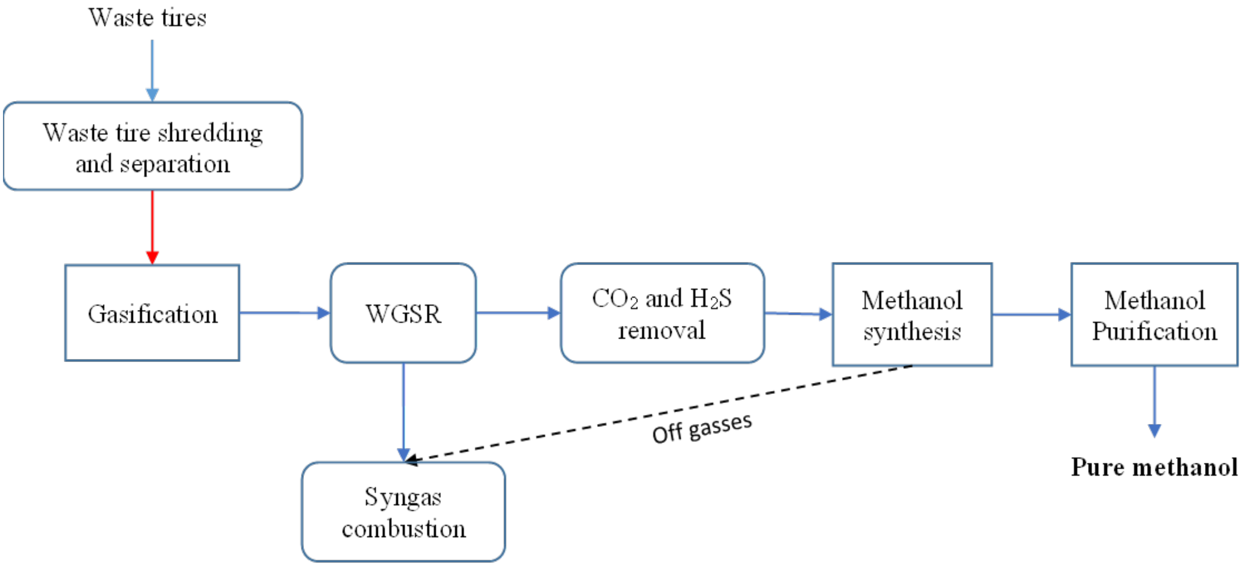

Figure 9.1. Waste tire to methanol and electricity block diagram.

9.2.1 Methanol Aspen plus flowsheet

9.2.1.1 Gasification

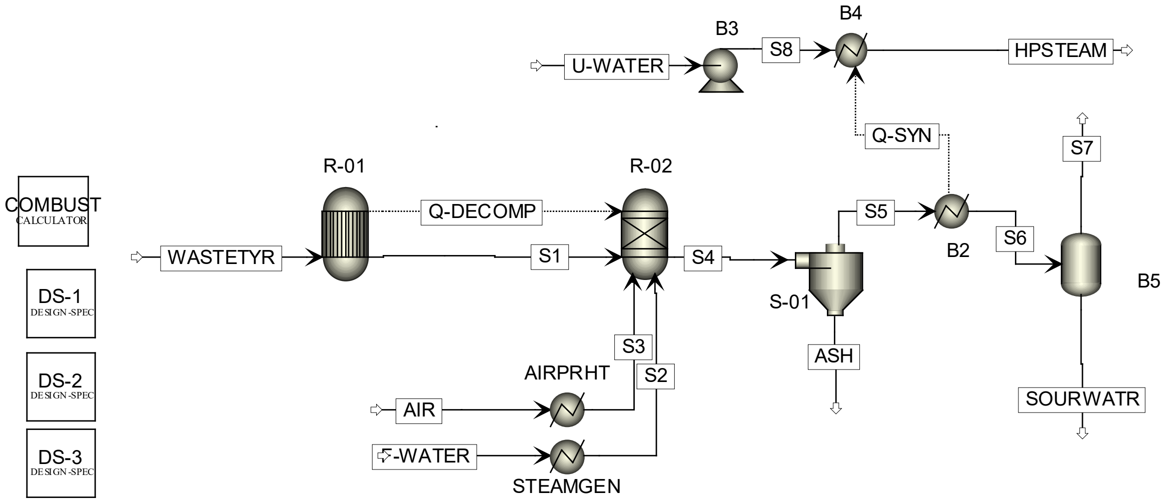

Figure 9.2. Gasification unit.

There are many different types of gasifiers, all of which are designed for specific types of materials. Here a downdraft gasifier configuration is chosen for its ability to crackdown tar formation thus reducing the need for downstream tar reforming steps. Tires are known to produce high amounts of tar, thus a high-temperature slurry-fed downdraft gasifier operating at 1000°C and 1 bar, is modeled using Aspen Plus RYield and RGibbs reactor models, a cyclone and heat exchanger. The method used follows that described by Aspen Plus solid tutorial. The feed of waste tires enters the RYield reactor where a Fortran calculator is used to decompose the non-conventional feed to its conventional elements according to the ultimate and proximate analysis described in Table 9.1.

The density and heat of the formation of tires are estimated using the Aspen Plus Coagist and Hgoalgen models that make use of the Beiu correlations. The conventional elements enter the RGibbs reactor where they react with air and steam to form syngas and light hydrocarbons. All the reactions are a combination of elemental components giving desired products [13]. The Gibbs reactor uses the Gibbs energy minimization method, which finds the most stable phase combination and seeks the phase composition where the Gibbs energy of the system reaches its minimum at a fixed mass balance, constant temperature, and pressure [14]. The gasifier was modeled to meet the target set in the previous paper [8,9,15]. A set of design specifications on aspen plus are set such that the gas composition H_2/CO is 1.44 and the temperature is 1000 °C.

The outlet from the GASIFY enters the CYCLONE which separates the ash from the syngas. A heat recovery system is used to recover heat from the gas stream. High-pressure steam is generated in the radiant syngas cooler and the gas is cooled to > 100 °C. The syngas is further quenched with water cooling the gas to 40 °C. A simple flash drum is used to simulate the removal of sour water. The clean gas is then sent to the water gas shift. For direct power production, the syngas is sent directly to the power generation unit.

Figure 9.2 shows the gasifier unit flowsheet. The performance of the gasification unit is measured using the lower heating value (LHVg), cold gas efficiency (CGE), and carbon efficiency ($\eta_{c,eff}$). These are calculated using the following equations taken from [16–18].

$$\mathrm{LHV_{gas}} = 10.789_{y_{H2}} + 12.625_{y_{CO}} + 35.818_{y_{CH4}} + 56.044_{y_{C2H2}} + 59.034_{y_{C2H4}} \quad \text{(eq.1)}$$

$$\mathrm{CGE} = \frac{\mathrm{LHV_{gas}} \times \dot{V}_{\mathrm{gas}}}{\mathrm{LHV_{feed}} \times \dot{m}_{\mathrm{feed}}} \quad \text{(eq.2)}$$

$$\eta_{c,eff} = \frac{\mathrm{Carbon_{product}}}{\mathrm{Carbon_{tires}}} \quad \text{(eq.3)}$$

Where $\mathrm{LHV_{gas}}$ and $\mathrm{LHV_{feed}}$ are the low heat value of the syngas (MJ/m^3) and waste tire feed (MJ/kg) respectively. $\eta_{c,eff}$ is the ratio of moles of carbon in the gaseous product stream (to the moles of carbon in the solid feed [16].

Table *9.3* shows the gasification unit operation conditions as well as the composition of the gas leaving the gasifier island.

Table 9.3. Gasification operating conditions and syngas composition.

Facility	Parameter	value	units
Gasifier	Entrained flow gasifier		
	Waste tire flowrate	6.37	kg/s
	Thermal input	216.58	MW
	Temperature	1050	C
	Pressure	1	bar
	oxygen/waste tire	0.88	kg/kg
	steam/waste tire	1.64	kg/kg
	RGIBBS reactor model for both gasifiers		
Cyclone	Cyclone-Modeling the gas and solid particle separation		
heat-exchanger	Steam boiler		
	Temperature	520	C
	HP steam	120	bar
Syngas		**20.0366**	**m^3/s**

H_2	45.99	%
CO	31.78	%
CO_2	18.08	%
H_2O	0.031	%
CH_4	0.00015	%
Syngas LHV	179.82	MW
CGE	83	%

9.2.1.2 Water gas shift (WGS)

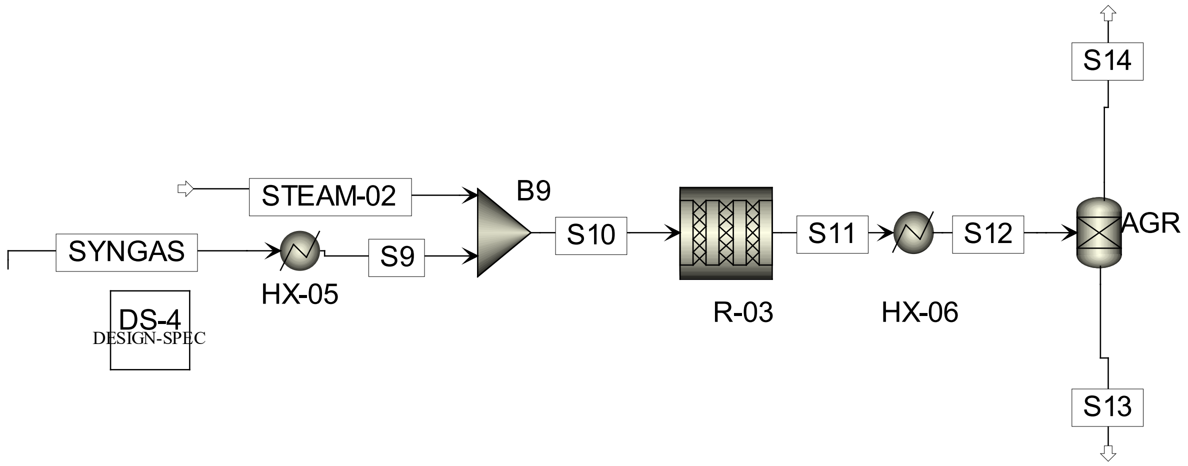

Figure 9.3. Water gas shift process unit.

The syngas ratio of H_2/CO is the most critical parameter affecting chemical synthesis processes. For the methanol synthesis, the ratio of H_2/CO should range from 2 to 2.1 and an excess of 3 for ammonia production. The ratio of H_2/CO in the syngas from the gasifier is 1.44, equal to the target in describe in Chapter 3. The H_2/CO ratio needs to be adjusted in a WGS reactor unit before entering the synthesis reactors. Steam is reacted with CO to create more H_2 in the syngas according to the water-gas shift reaction:

$$CO + H_2O = CO_2 + H_2 \quad \text{(eq.4)}$$

Figure 9.2 shows the waster gas shift process unit. The WGS is modeled as a sour gas shift reactor (SWGS) in that it also includes COS hydrolysis to H_2S. High-pressure steam from the radiant syngas is used for the high-temperature gas shift reaction as shown in equation (4). Since there is no change in the number of moles in the WGS, the pressure is maintained at 1 bar and 350 ºC [19]. A design spec in Aspen Plus is used to obtain the desired H_2/CO ratio. We use a plug flow reactor (RPlug model) in Aspen Plus to simulate the WGS reactor. The reaction is exothermic and solid-catalyzed. The reaction kinetics for this unit are those developed by

Bussche & Froment [20] and described by the LHHW-type equations (Langmuir-Hinshelwood- Hougen-Watson) in the form suitable for the Aspen Plus ® application [21]. The kinetic structure of the LHHW in this work has the form [20–22]:

$$R = (\text{kinetic term})\frac{\text{driving force}}{\text{adsorption term}} \qquad \text{(eq.6)}$$

Equation 7 shows the reaction rate and kinetic and adsorption data entered in the Aspen Plus ® LHHW reaction model [20–22].

$$R_{WGS} = \frac{k'_1 p_{CO_2}\left[1-k'_3\left(\frac{p_{H_2O}p_{CO}}{p_{CO_2}p_{H_2}}\right)\right]}{\left[1+k_3\left(\frac{p_{H_2O}}{p_{H_2}}\right)+k_1\sqrt{p_{H_2}}+k_2 p_{H_2O}\right]} \qquad \text{(eq.7)}$$

For every mole of CO shifted 1 mole of CO_2 is produced. Thus, a large percentage of the exit syngas from the WGS is CO_2. The composition of the shifted syngas is shown in Table 9.4

Table 9.4. Composition of syngas.

Syngas composition	
Flowrate (kmol/hr)	3190.49
H_2	0.662
CO	0.315
CO_2	0.016
H_2O	0
CH_4	1.91E-06
Syngas LHV	180.36
CGE (%)	83.28%

9.2.1.3 Syngas Cleaning

The raw syngas leaving the WGS contains a significant amount of CO_2, H_2S, and other contaminants and need to be removed prior to downstream processing of the gas. They are dangerous to the catalyst used to synthesize chemicals/fuels and corrosive to combustion turbines and other downstream equipment. Therefore, syngas needs to go through several cleaning and conditioning steps to reduce the contaminants. The MDEA solvent is used to remove 100% of H_2S and 95% of CO_2. For the sake of simplicity, the unit is assumed to consume 3.5% of the total thermal input [23].

9.2.1.4 Methanol Synthesis and distillation

The chemical reaction to produce methanol causes a decrease in the number of moles in the system, thus the reaction is favored at elevated pressures as shown in Figure 9.4 that the production of methanol increases with pressure and reaches a plateau at pressures above 110 bar. Therefore, an RPlug reactor operating at 220 ºC and 110 bar to convert the syngas to methanol is modeled. A kinetic model for the hydrogenation of CO and CO_2 to methanol on a commercial $Cu/ZnO/Al_2O_3$ catalyst is implemented according to the approach suggested in [20] and followed in [10,21]. Bussche and Froment [20], showed that the carbon conversion to methanol is highest when the concentration of CO_2 in the feed is about 3-5%. The concentration of CO_2 in the feed is reduced to 5% through syngas gas cleaning. Figure 9.5 shows the syngas to methanol process. Clean syngas is compressed through a series of three compressors with intermediate cooling. The syngas is heated to 150 ºC and enters the methanol synthesis reactor at 110 bar. The packed tubular reactor has 6000 tubes with a length of 14 m and a diameter of 0.03 m. The reactor temperatures increase from 150 ºC to 260 ºC and the effluent exits the reactor at 220 ºC. The reactor is cooled by generating high-pressure steam at 230 ° and 30 bar. The kinetic data used for the Rplug reactor are in the form of LHHW as described in [7,20–22,24].

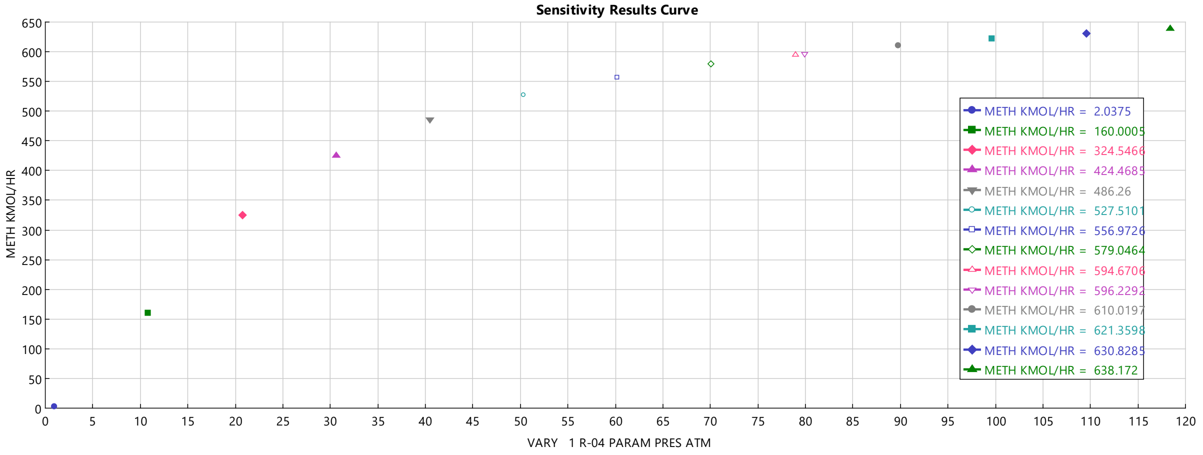

Figure 9.4. Effect of the pressure on methanol yield.

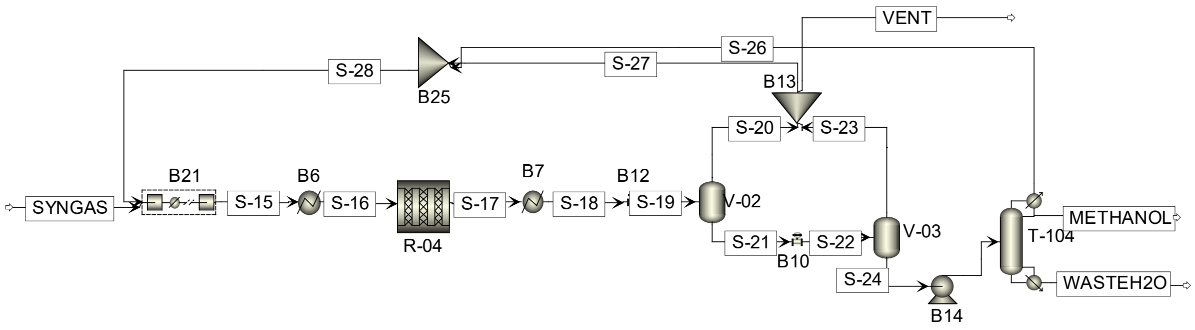

Figure 9.5. Methanol synthesis and distillation.

$CO_2 + 3H_2 = CH_4O + H_2O$ (eq.8)

$CO + H_2O = CO_2 + H_2$ (eq.4)

$$R_{WGS} = \frac{k_5\ p_{CO_2}\left[1 - K'_{E1}\left(\frac{p_{H_2O}p_{CO}}{p_{CO_2}p_{H_2}}\right)\right]}{\left[1 + k_3\left(\frac{p_{H_2O}}{p_{H_2}}\right) + k_1\sqrt{p_{H_2}} + k_2 p_{H_2O}\right]} \quad \text{(eq.7)}$$

$$R_{CH4O} = \frac{k_4\ p_{CO_2}p_{H_2}\left[1 - K''_{E2}\left(\frac{p_{CH_3OH}p_{H_2O}}{p_{CO_2}p^3{}_{H_2}}\right)\right]}{\left[1 + k_3\left(\frac{p_{H_2O}}{p_{H_2}}\right) + k_1\sqrt{p_{H_2}} + k_2 p_{H_2O}\right]^3} \quad \text{(eq.9)}$$

Where:

$$k_1 = 3453.38$$

$$k_2 = 0.499 \exp\left(\frac{17197}{RT}\right)$$

$$k_3 = 6.62 \times 10^{-11} \exp\left(\frac{124119}{RT}\right)$$

$$k_4 = 1.07 \times 10^{-3} \exp\left(\frac{36696}{RT}\right)$$

$$k_5 = 1.227 \times 10^{7} \exp\left(\frac{-94765}{RT}\right)$$

$$K'_{E1} = 4.4724 - 4400/T$$

$$K''_{E2} = -24.389 + 7059.726/T$$

The product stream from the methanol synthesis reactor, which consists of unreacted syngas, water, methanol, and other inert gases, is cooled to 35 degrees Celsius and fed to a succession of flash drums kept at various pressures in order to purify the methanol. The methanol-rich liquid stream from the final flash drum is sent to a distillation column operating at 2 bar and 110 degrees Celsius. In the distillation column, the methanol-rich liquid is purified to 99.9% (vol/vol). To maximize the carbon-to-methanol conversion, the syngas recovered in the vapor outputs of the flash columns are recycled back to the methanol reactor. Inert gases such as methane and nitrogen in the synthesis gas fresh feed are eliminated from the system by purging a small portion of the recycled vapor.

9.2.1.5 Power generation unit

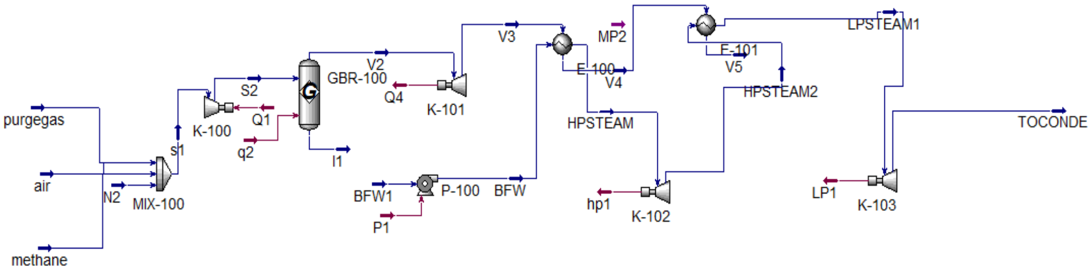

Figure 9.6. Power generation unit using off-gases.

The purge gases from the methanol column are sent to the gas turbine for combustion and generate electricity as shown in Figure 9.6. The purge gases consist of unused syngas, methane, and small amounts of methanol. The exhaust gases from the turbine are fed to a heat recovery steam generation unit which together with the surplus heat from the above process units is converted to steam which is used to generate electricity in a steam turbine.

overall energy efficiency,

$$\eta_{\text{energy}} = \frac{\text{product}_{\text{LHV}} + \text{output Power}}{\text{tire feed}_{\text{LHV}} + \text{utilities}} \qquad \text{(eq. 10)}$$

9.2.2 Simulating the IGCC

During IGCC operation the Methanol synthesis reactor is bypassed. The syngas from the gasification unit is cleaned and sent directly to the turbine where the gas is combusted in the gas turbine for electricity. The exhaust gases are used to generate more work through the heat recovery steam generation with three steam pressures. The operation of the gas turbine is shown in

Table *9.5* and Figure 9.7. The PRBM method is adopted for material property analysis while STEAMNBS is employed for steam and water facilities including ST and pumps.

Table 9.5. Combined cycle power plant operating parameters.

Pressure ratio	30	bar
Temperature	1300	°C
Isentropic efficiency	90	%
Steam cycle		
HP	120	bar
MP	30	bar
LP	3	bar
HP, MP, LP temperature	460, 385, 137	°C
Isentropic efficiency	90	%

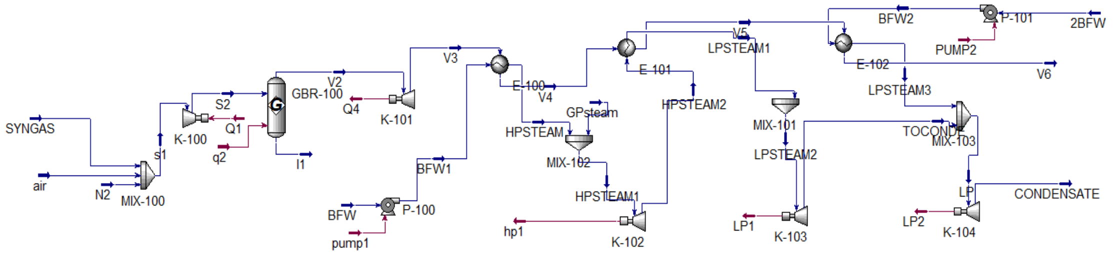

Figure 9.7. Combine cycle power plant.

9.2.3 Economic analysis

The process modeling results were used to estimate the total capital investment (TCI) and the operating costs in $/ton of waste tire for the two processes. The process profitability is assessed using the Net present value (NPV) which is the difference between the present value of cash inflows and the present value of cash outflows over a period of time and it is calculated based on the following equation.

$$\mathrm{NPV} = \sum_{t=0}^{n} \frac{\mathrm{Rt}}{(1+\mathrm{r})^{\mathrm{t}}} - \mathrm{R_o}$$

Where Rt is the annual cash flow, being the difference between Revenues (R) and Expenditures, Operation, and Maintenance Costs. r is the discount rate and Ro is the total capital costs of investment and is the lifetime of the investment. The actual selling price of methanol and electricity was estimated by setting the NPV equal to \$0. A zero-based net present value indicates that the project has no profit, nor does it have any losses incurred over the course of its lifetime. The NPV is essentially the offset that is calculated between the amount of money invested in the project, the future benefits, and the final values of the project's lifetime. A positive net present value indicates that the project if carried out, will result in a profit. If, on the other hand, an NPV is negative, indicates that the business model does not generate a profit [25].

9.2.3.1 Equipment costing

The costing and sizing of the equipment for the two processes were determined based on the results of the process modeling, which included the composition, flow rate, temperature, pressure, and enthalpy of the various streams. Some of the units were handled as packages, and their sizes were determined according to the flow rates of the feeds they received. Table 9.6 shows the turn-key equations used to calculate the capital cost of each of the main units. The capital costs of other different pieces of equipment such as tire pretreatment and crumbing are estimated from data available for similar processing units in established literature sources considering the Chemical Engineering Plant Cost Index (CEPCI). The following equation is used to determine the present desired values.

$$C_{new} = C_{old} \cdot \left(\frac{S_{new}}{S_{old}}\right)^{\tau} \times \frac{CEPCI_{new}}{CEPCI_{old}}$$

where, C_{old} and C_{new} are the cost of the known scale and desired scale, respectively; S_{old} and S_{new} are the known scale and desired scale, respectively; τ is the power scaling factor. The initial working capital is assumed to be 5% of the equipment and installation cost while the land is assumed to be 2% of the equipment and installation cost since land in South Africa is relatively cheaper compared to the more developed world.

Table 9.6. Turnkey cost (TKC) equation and cost functions for the two cases

Unit operation	**Costing equation**	**Reference**
Gasification unit	$= \frac{\text{C.E.Index}}{361.3} \cdot 316{,}800 \cdot \left(\frac{\text{feed}}{\text{1ton/day}}\right)^{0.7}$	[26,27]
ASU	$= \frac{\text{C.E.Index}}{332} \cdot 23116{,}000 \cdot \left(\frac{\text{Oxygen flow}}{\text{3900.1 kmol/hr}}\right)^{0.6}$	[26,27]
Cyclone, scrubber WGS, AGR,	$= 54.3 \times 10^{6} \cdot \left(\frac{\dot{m}_{\text{syngas}}}{\text{13400kg/hr}}\right)^{0.65}$	[28,29]
Combined cycle power plant	$= \frac{\text{C.E.Index}}{392.6} \cdot 40000000 \cdot \left(\frac{\text{Total Net Power}}{\text{69 MW}}\right)^{0.7}$	[26,27]
Compressor, Methanol synthesis reactor, and distillation unit	$= 14.2 \times 10^{6} \cdot \left(\frac{\dot{m}_{\text{syngas}}}{\text{54000 kg/hr}}\right)^{0.65}$	[28–30]

9.2.3.2 Operating Costs

The results of the process modeling were used to estimate the annual operating cost, which comprises labor, consumables such as chemicals and catalyst and solvent makeup, utilities, maintenance, sales, administrative support, and overhead costs, as well as insurance and taxes. The estimate of annual consumptions was based on an operational factor of 8000 hours per year. It was estimated that the labor cost for the methanol process would be 19000 dollars per year, which is equivalent to R350 000, with a total staff of 120 people, whereas the IGCC facility would require 110 workers. It was expected that the expenditures associated with maintenance would amount to 4% of the overall cost of installation (TCI). It was estimated that the costs associated with administration and support would make up 40% of the total amount spent on labor and maintenance, while the costs associated with insurance and taxes would make up two percent of the total cost of installation. In addition, the annual cost of the catalyst, solvents, and other running supplies was combined as operating supplies and approximated to be 2% of the total cost of installation. The utilities account for 10% of the total equipment cost (excluding land and working capital). Table 9.7 provides an overview of the most significant financial parameters considered in the modeling procedure.

9.3 Results and discussion

9.3.1 Performance analysis

This section presents the results of energy and economic analysis. The main parameters in energy and economic analysis are the process's overall efficiency and total capital investment and minimum selling price. Table 9.8 provides the performance analysis and the required capacity of each process unit. The capacities in Table 9.8 are also used to estimate the cost of packages based on delivery to the site (turnkey cost, TKC), based on the equations in Table 9.6. The methanol route achieved an overall net thermal energy efficiency of 47.12 % compared to 37.32% achieved in the IGCC route. The methanol route also provides savings in carbon emissions. By producing methanol, the carbon that would lead to CO_2 emissions is diverted to methanol. The carbon efficiency from waste to methanol was 49.87%, whereas all carbon in the IGCC routs is converted to CO_2. However, the methanol route requires an additional amount of energy since the off-gases (purge gas) combustion does not provide the sufficient energy required to reach the compressive pressure of 110 bar for the methanol synthesis reactor. The energy is supplied either by procuring electricity or by supplementing it with methane. When methane is used to supplement the energy needed, the carbon efficiency drops from 49.87% to 40.60%. Thermal efficiency also dropped from 52.29% to 47.12%. Despite this, the methanol routes still provide better performance that the IGCC. Alternative methods can be utilized to deliver the required energy, solar energy, burning additional tires, or diverting some of the syngas to combustion. However, this is lower than the targets set in [15] where the carbon efficiency was 54.5%, the current methanol route achieved a carbon efficiency of 49.87% (waste tire to methanol). The conversion of syngas to methanol is a function of pressure, and then in the Aspen plus at a pressure of 110 bar, the conversion of CO to methanol is 0.8, whereas in [15] a 100% conversion was assumed. The Aspen Plus flowsheet is close to the real process that the flowsheet in [15] showed the limit of performance.

CO_2 emissions are another important parameter in comparing and investigating the efficiency of the two processes. It is defined as the ratio between the produced CO_2 over the ton of waste tire feed. The methanol route supplemented with methane produced 2.05 kg CO_2 per kg of waste tire feed compared to 2.8 kg CO_2 per kg of tire feed.

Table 9.7. Key economic parameters

Economic parameters	
Basis year for analysis	2020
Waste tire	Free
Supplement methane price	5$/GJ
Methanol Price	$400/ton
Electricity price	$0.078/kWh
CO_2 emissions	$8 /ton
Waste disposal	18
Water	$0.002/l
Plant life	20 yrs
Annual operating hours (hr)	8000
Equity %	50.0%
Loan %	50.0%
Loan interest rate	8.0%
Loan term, yrs	10
Discount rate %	10.0%
Income tax rate %	28.0%
Depreciation period (yrs)	10
Inflation %	8.00%
Construction Period (yrs)	3
Purchasing Power Parity	1
Land	2% of equipment and installation cost
Working capital	5% of equipment and installation cost
Fixed operating costs	
Direct labor	$19000/person
Maintenance salaries	1% of total capital investment cost
Administrative, support & overhead cost	40% of direct labor cost
Fringe benefits	30% of operators, maintenance,
Operating supplies	1% of total capital investment cost
Insurance and taxes	2% of total capital investment cost

Table 9.8. Performance analysis.

Plant Data	Unit	WT-Methanol-P	WT-P
Thermal input	MW	216.58	216.58
waste tire flowrate	kg/s	6.37	6.37
Supplementary Thermal input	MW	75	0
Additional methane	kg/s	1.5	0
	Chemical production		
Methanol	MW	132.1	0
	Power generation		
Gas Turbine	MW	27.83	70.05
Steam Turbine	MW	14.01	29.53
Total output power	MW	41.84	99.58
	Power consumption		
Pumps	MW	0.09	0.30
Compressors	MW	18.10	0.043
AGR	MW	7.58	7.58
ASU	MW	10.83	10.83
Total power consumption	MW	36.60	18.757
	Main output		
Gross thermal output	MW	173.98	99.58
Net output	MW	137.38	80.82
Net thermal Efficiency	%	47.12	37.32
CO_2 emissions	$kgCO_2$/kg tire	2.04	2.82

9.3.2 Economic performance

Table 9.9 provides a summary of the overall capital investment based on an estimation of the capital cost associated with each process unit. The TCI that was computed for WT-methanol-E (methanol purchasing electricity), WT-P (IGCC), and WT-methanol-P (methanol-methane) and came out to be 136.37 million dollars, 211.30 million dollars, and 182.16 million dollars, respectively. The capital investment needed for the IGCC is greater than that of methanol because of the increased capacity of the combined cycle power plant. Table 9.9 further summarizes the operational costs for WT-methanol-E (methanol-additional electricity), WT-P (IGCC), and WT-methanol-P (methanol-additional methane).

To determine the operational cost, the methanol selling price was initially believed to be \$400/ton, while the minimum selling price for electricity was 0.078\$/kWh. These figures are based on current market conditions. The cost of power in South Africa is 0.078 kWh, and because the region competes with Asia Pacific, where the methanol price is 395 \$/ton, a price of \$400/ ton was used to determine the OPEX. WT-methanol-E, WT-P, and WT-methanol-P had total annual OPEX of 57.18 M$, 49.17M$, and **55.70** M$, respectively. WT-methanol-E had an 8.1 M$ higher expense than WT-P and only 1.48 M$ higher than WT-methanol-P. To compare the created designs, the net present value (NPV) was used in the analysis. All the configuration has negative NPV based on the assumed minimum selling price (WT-methanol-E: -$65.14. WT-P: -$208.1, WT-methanol-P: -$60.46). Therefore, none of the processes can produce profit, or be investable at these product prices. The impact of waste tire levies on minimum selling prices of methanol and electricity prices on net present value (NPV) are presented in the sensitivity analysis section [12].

9.3.3 Sensitivity analysis

Figure 9.8 shows the impact of the minimum selling price on methanol on WT-Methanaol-E and WT-methanol-P designs producing methanol resulting in an NPV of 0 $. The minimum selling price of methanol, for the two processes, is $420 /ton. Any price above this value would lead to profits for the two processes. Figure 9.9 shows the impact of the minimum selling price of electricity for WT-P designs resulting in an NPV of 0 $. The price of electricity should be above 0.098 $/kWh to make the IGCC process investment ready. Currently, the South African state-owned utility Eskom has a purchase agreement with independent power producers where it procedures additional electricity at prices ranging from 0.109 to 0.272 $/kWh over 20 years. Therefore, is enough potential for the process to generate profit. The other way to make these processes profitable is to consider the tire levies as direct revenue. Figure 9.10 shows the impact of the tire levy on the minimum selling price. The waste tire levy in South Africa is R2.31/kg (0.132 $ /kg) of which only R0.31/kg (0.0177 $/kg) is given to processes that handle over 1000 tonnes. Increasing the levy paid to processes greatly impacts the selling price. Increasing the tire levy from 0.0177$/kg to 0.115 $/kg, the IGCC and methanol processes have profit with NPV of $39.99 and $164.17, respectively. Therefore, producing methanol has better financial performance than the IGCC route.

Table 9.9. Results of the economic optimization

Capital expenditure				
	WT-Methnol-E	WT-P	WT-Methanol-P	
Tire pretreatment	23.25	23.25	23.25	M$
Downdraft gasifier	43.33	43.33	43.33	M$
ASU	13.79	13.79	13.79	M$
Cyclone, Tar cracker &WGS and AGR	38.58	38.58	38.58	M$
CCPP	0.00	78.53	42.80	M$
Methanol synthesis + distillation	8.50	0.00	8.50	M$
Land	2.55	3.95	3.39	M$
Working capital	6.37	9.87	8.51	M$
Total Capital Investment costs	**136.37**	**211.30**	**182.16**	M$
Operating expenditure				
Direct Wages	1.97	2.09	2.28	M$
Administration	2.75	3.79	3.45	M$
Fringe benefits	2.88	3.98	3.63	M$
Operating supplies	2.73	4.23	3.64	M$
Maintenance cost	4.77	7.40	6.38	M$
Insurance and taxes	2.73	4.23	3.64	M$
Plant overhead	1.46	1.46	1.60	M$
CO_2 emissions TAX	1.96	4.14	3.01	M$
Waste disposal	0.22	0.22	0.22	M$
Utilities	12.74	19.75	17.02	M$
Electricity cost	22.84	0.00	0.00	M$
Methane cost	0.00	0.00	10.80	M$
Total operating costs	**57.18**	**49.17**	**55.70**	M$
Revenues				
Methanol selling	75.42	0.00	75.42	M$
Selling electricity	0	62.14	3.27	M$
Total revenue (100% capacity)	75.42	62.14	78.69	M$
Total revenue (85% capacity)	64.10	52.82	66.88	M$
Gross earnings (85%) capacity	**6.92**	**3.64**	**11.19**	M$
NPV	**-$65.14**	**-$208.1**	**-$60.46**	**M$**

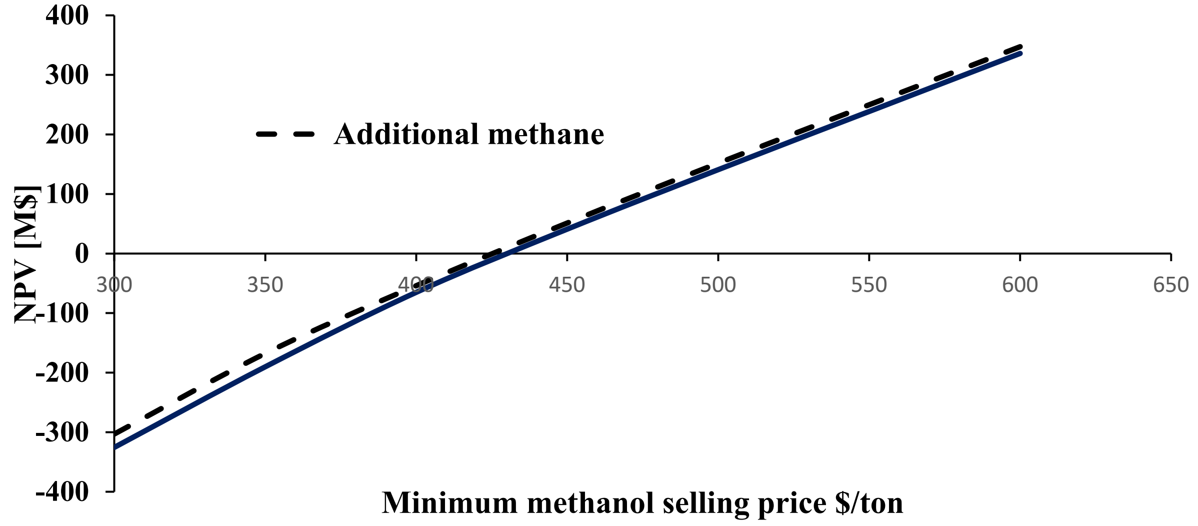

Figure 9.8. Impact of methanol minimum selling price on NPV

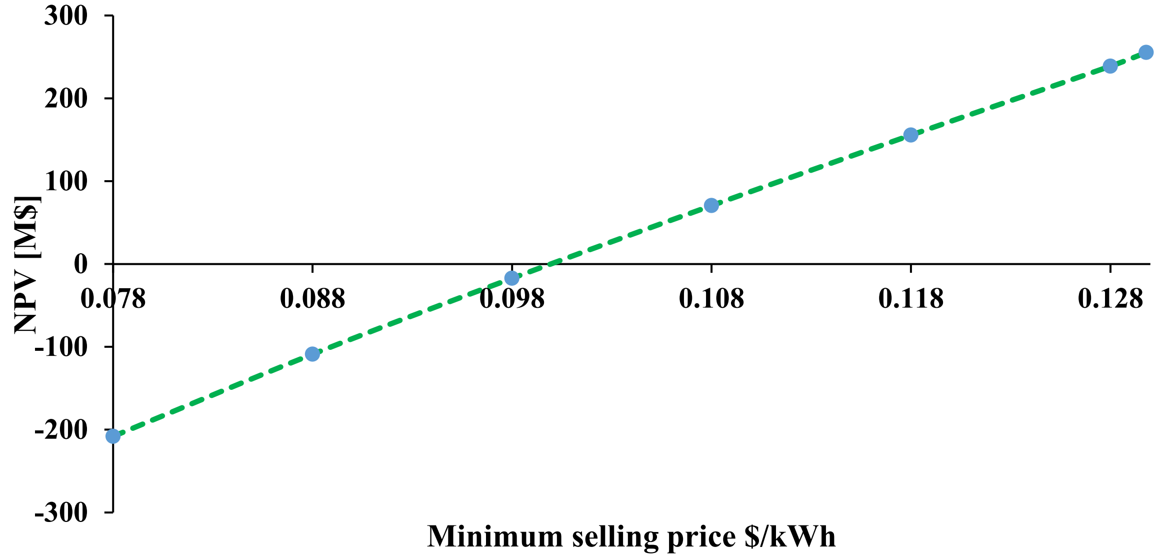

Figure 9.9. Impact of electricity minimum selling price on NPV

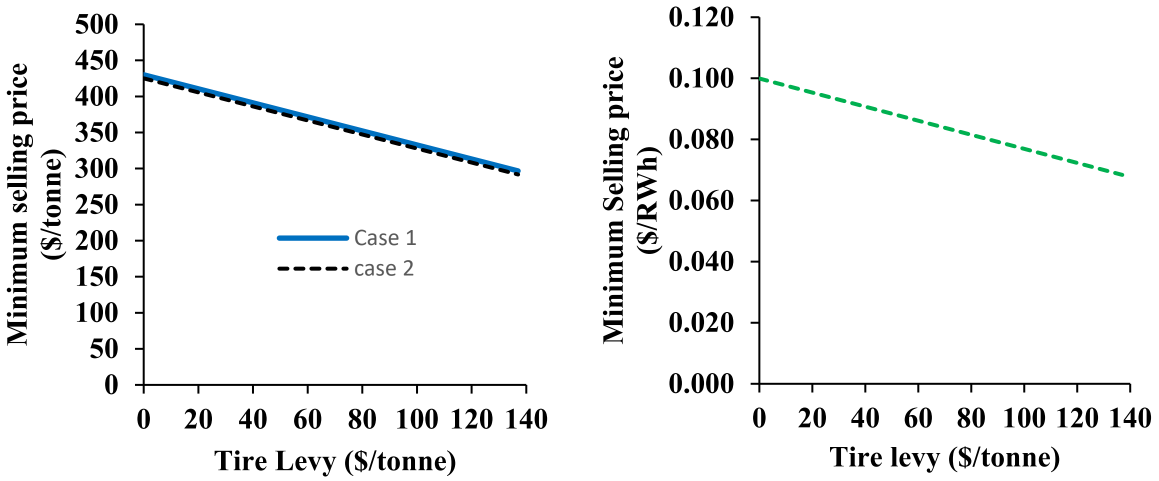

Figure 9.10. Impact of waste tire levies on the minimum selling price (a) methanol, (b) electricity.

9.4 Conclusion

The study examines the technological and economic feasibility of producing methanol and power from waste tires. This optimization was based on the goals established in Chapters 6 and 7. Two process models were created in Aspen Plus ® and Aspen Hysys ®, where the base WT-methanol-P was the production of methanol and electricity with an additional supply of methane. The other was WT-P, which was the exclusive conversion of waste tires to energy. WT-methanol-E was an alternate technique that produced methanol but required additional electricity for compression. WT-methanol-P had a greater thermal efficiency of 47.12% than WT-P, which had 37.32%. When compared to WT-P, CO_2-specific emissions in WT-methanol-P were reduced by 0.78 kg CO_2/kg tire feed (780-kilogram CO_2/ton of tire). This meant producing methanol has significant carbon emissions saving power production only. The economic analysis revealed that the total investment cost for a ton of waste tire (TCI/ton of tire) in WT-P was 1051 \$/ton and 907 \$/ton in WT-methanol-P. Furthermore, the minimum selling prices of methanol were discovered to be 430 \$/ton and 0.098 \$/kWh for power, both of which are within the range of current market values. We also observed that tire tipping fees significantly affect the minimum selling price. The minimum levy necessary to make the processes economical is 0.115 \$/kg.

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10 Conclusion and recommendations

In this work, waste tire thermochemical conversion to chemicals and energy was explored using theoretical techniques and experimental techniques. Waste tires contain an energy content comparable to coal and higher than that of biomass. Yet this energy resource remains unused, dumped in landfills or storage depots with no reuse plan. In this study, the thermodynamic properties of G and H were utilized to generate various process flowsheets with the overarching objective of minimizing carbon emissions and reducing work loss while preserving production capacity. The G-H was used to determine the attainable region for waste tire chemical conversion into various products. The attainable region provided information on the performance limits of the process from the material and energy perspectives. The limits of performance can be understood as the extreme points that any tire chemical conversion process can achieve. This was accomplished by applying the GH-space concepts to the synthesis of carbon dioxide-emitting technologies with a reputation for subpar performance. In particular, pyrolysis, gasification, methanol synthesis, and IGCC processes. Waste tires fall in the category of waste that is exceedingly difficult to recycle. Therefore, this work also contributed to experimental analysis and investigated the effect of parameters such as catalysts, temperature, and co-treatment with other feedstocks, to improve the thermochemical conversion of tires. The catalytic effect of spent FCC catalysts in CO_2-assisted gasification of waste tires was investigated for energy reclamation and as a channel for carbon usage. The effects of carbon dioxide were investigated by comparing the syngas produced during pyrolysis and CO_2 gasification of used tires. To better understand the catalytic activity of FCC, the effect of catalyst position (in-situ and quasi-in-situ) on syngas yield during CO_2, gasification was investigated to examine the role of catalyst contact with the solid phase and the volatiles from waste tires. To further examine the impact of catalytic activity against thermal enhancement on syngas yield and quality, the effect of temperature during catalytic CO_2 gasification of tires was also assessed. The synergy of the co-gasification of waste tires and gypsum in the CO_2 atmosphere was also examined experimentally, however since gypsum contains sulfur, thermodynamic equilibrium analysis using Gibbs free-energy minimization was used to investigate the sulfur redistribution between gases and condensed phases under different process conditions. The distribution of which is controlled by temperature and feeding ratios. Aspen Plus® (V12) code was used to understand this behavior. The effect of air ratio, and gypsum mass fraction, on syngas evolution and sulfur transformation, was investigated. This study was coupled with the evaluation of metal speciation and thus MSW was used as feedstock instead of tires. The following was found:

1. **Theoretical analysis**
    a. It was found that pyrolysis pathways perform better in terms of thermodynamic efficiency and carbon footprint than gasification processes, which lose about 45% of the carbon feed to carbon dioxide. However, the gasification routes offer higher potential revenue, yielding as much as \$625 per ton of waste tire as compared to \$205 from the pyrolysis route. Based on these results other alternative gasification routes that produce other chemicals and power were further analyzed in detail in the subsequent chapters of this dissertation. The process synthesis method used in chapter 3 forms the basis of all analysis since it established the potential of a process pathway in a universal way that is independent of the specifics of process design and optimization, thus making it possible to do long-range planning based on fundamental thermodynamics rather than the limitations of current process design. This approach is better suited to long-range planning, not only for research engineers but also for legislators and long-term investors, because it indicates prospects.
    b. Two quantities, thermal efficiency, and work efficiency were used to compare the performance of the three power plant routes. The results show that the IGCC system can conserve the chemical potential of waste tires. IGCC system developed here does not use oxygen or air during gasification and achieved a thermal efficiency of 45.65 % with a net-work output of 10.5 GJ/ton of tire which is much higher than that of conventional coal IGCC at 9.6 GJ/ton of coal.
    c. The limit of performance for the co-production of methanol and electricity from a fundamental thermodynamic perspective was investigated. For the system developed here a carbon efficiency of 54.6% and the chemical potential efficiency of 63% were achieved. Equally the system produced 2.42 GJ/ ton of waste tire and has the potential to generate a revenue of \$ 620/ton of waste tire. The study shows converting tires to electricity and methanol is achievable, however, 45% of the carbon resource will end up as carbon dioxide.
    d. The IGCC and methanol synthesis processes were optimized in Aspen Plus ® and Aspen Hysys ®, to conduct a detailed techno-economic analysis of these two processes. A process converting waste tire to methanol and power had a greater

thermal efficiency of 47.12% than IGCC, which had 37.32%. The IGCC CO_2-specific emissions were 0.78 kg CO_2/kg tire feed (780-kilogram CO_2/ton of tire) more compared to WT-methanol-P. This meant producing methanol has significant carbon emissions saving that producing power production only. The economic analysis revealed that the total investment cost for a ton of waste tire (TCI/ton of tire) for the IGCC was 1051 \$/ton while it was 907 \$/ton for the WT-methanol-P. Furthermore, the minimum selling prices of methanol were discovered to be 430 \$/ton and 0.098 \$/kWh for power, both of which are within the range of current market values. We also observed that tire tipping fees significantly affect the minimum selling price. The minimum levy necessary to make the processes economical is 0.115 \$/kg.

2. **Experimental analysis**
    a. The addition of gypsum in used tires improved the quantity of syngas produced by converting char and tars. The addition of gypsum to waste tires also improved the quality of the syngas by increasing the energy yield of the syngas. With the addition of gypsum, the overall production of syngas increased by up to 55 percent, while the energy yield (MJ/kg of feedstock) increased by 40 percent. With the addition of gypsum, the product gas yield, energy, and H_2 and CH_4 yields rose, whereas the CO yield increased only at lower gypsum concentrations.
    b. The results also indicate that the addition of spent FCC catalyst increased the yields of syngas and energy. CO_2-assisted gasification produced greater quantities of CO-rich syngas than pyrolysis. Compared to in-situ catalytic gasification, quasi-in-situ gasification raised syngas and energy yields by 24% and 23%, respectively, indicating that quasi-in-situ catalytic gasification is more efficient and effective for increasing syngas yields. Raising the temperature to 950 degrees Celsius improved the yields of syngas and energy as a result of enhanced reforming and cracking reactions. Using spent FCC catalyst improves the economics of waste management for FCC facilities while simultaneously enhancing the energy recovery from waste tires.
    c. Equilibrium analysis of sulfur transformation when gypsum is added revealed that the transformation of gypsum sulfur to SO_2 can be prevented with the reactor temperature kept < 1050 °C. SO_2 production can be prevented if the carbon to gypsum mass ratio is kept below < 33 wt.% and the air ratio (λ) < 0.4. Adding 9 wt.% gypsums reduced H_2 and CO by 10% and 12%, respectively whilst CO_2

increased by 51%. Gypsum decomposition proceeds via ($CaSO_4 + 2C \rightarrow CaS + 2CO_2$) and ($CaSO_4 + 4C \rightarrow CaS + 4CO$). The first reaction dominates at high oxidative and low gypsum mass fractions environments. The main reaction involved in the production of SO_2 is ($2CaSO_4 + C \rightarrow 2CaO + 2SO_2 + CO_2$).

3. **Prospects for future study**
   a. Detailed techno-economic studies that benchmark the waste tire thermal conversion processes to the reuse and material recycling processes.
   b. Experimental studies to validate the method developed in this study:
      i. Gasification of tires coupled with methanol synthesis.
      ii. Iron ore reduction using waste tires.
      iii. Methanol synthesis using formulated syngas based on the results presented in chapters 4 and 5.
      iv. Life cycle analysis of methanol and hematite reduction will be conducted.
   c. Continuation of this work, which is to use GH-space to analyze the co-gasification of various waste materials and evaluate existing flowsheets to determine how these processes might be improved to minimize carbon emissions and energy loss.
   d. Continuation of gasification of waste tires with spent FCC catalyst, investigating the influence of steam, oxygen, and temperature.
   e. Continuation of catalytic co-gasification of waste tires and other feedstocks such as plastics for a polygeneration system to meet the demand.