LIQUID FUEL PRODUCTION FROM PYROLYSIS OF WASTE TIRES:

PROCESS SIMULATION, EXERGETIC ANALYSIS,

AND LIFE CYCLE ASSESSMENT

by

Ryan K. Altayeb

A Thesis Presented to the Faculty of the
American University of Sharjah
College of Engineering
in Partial Fulfillment
of the Requirements
for the Degree of

Master of Science in
Chemical Engineering

Sharjah, United Arab Emirates

June 2015

Approval Signatures

We, the undersigned, approve the Master's Thesis of Ryan K.Altayeb.

Thesis Title: Liquid Fuel Production from Pyrolysis of Waste Tires: Process Simulation, Exergetic Analysis, and Life Cycle Assessment

Signature	**Date of Signature** (dd/mm/yyyy)
_____	_____
Dr. Taleb Ibrahim Professor, Department of Chemical Engineering Thesis Advisor	
_____	_____
Dr. Ahmed Aidan Laboratory Instructor, Department of Chemical Engineering Thesis Co-Advisor	
_____	_____
Dr. Nabil Abdel Jabbar Professor, Department of Chemical Engineering Thesis Co-Advisor	
_____	_____
Dr. Salwa Beheiry Associate Professor, Department of Civil Engineering Thesis Committee Member	
_____	_____
Dr. Hussain Ahmed Professor, Department of Chemical Engineering Thesis Committee Member	
_____	_____
Dr. Naif Darwish Head, Department of Chemical Engineering	
_____	_____
Dr. Mohamed El-Tarhuni Associate Dean, College of Engineering	
_____	_____
Dr. Leland Blank Dean, College of Engineering	
_____	_____
Dr. Khaled Assaleh Director of Graduate Studies	

Acknowledgements

Dedication

This humble effort is dedicated to my mother and father, for their unconditional love and endless support; without their patience and understanding this work would not have been possible. Also, it is dedicated to my sisters (Salma, Samah, Suhyla and Dania) and my brother Ahmed who always surround me with love and support. To my friends, family and colleagues who believed in me and continuously give me the power to proceed.

Abstract

Scrap tire is considered to be one of the very common and significant solid wastes and its production is increasing due to the increased number of vehicles in both developed and developing countries. Initiatives are being taken to overcome the fossil fuel crisis by looking for alternatives to replace gasoline and diesel fuel. This work presents the simulation of waste tires pyrolysis process in ASPEN Plus$^{®}$ 8.4 where the effect of temperature on the pyrolytic oil yield was investigated. It is shown that the optimum temperature for waste tire pyrolysis in a rotary kiln reactor is around 450-550°C. Also, an exergetic analysis of the pyrolysis reactor was performed to study the performance of the process. The overall exergetic efficiency of the reactor was found to be 69.9% which is equivalent to an exergy destruction of 30.1% due to process irreversibility. Finally, life cycle assessment of the process using SimaPro 7.3.2 was conducted to find out if the process of waste tire pyrolysis is environmentally friendly. The results showed that the pyrolysis process can be considered environmentally friendly but there is room for improvement. A sensitivity analysis was conducted to investigate the effect of changing the heating fuel in the process where non-condensable gases produced in the process were utilized for heating purposes. The results showed a significant reduction on the environmental impacts due to the reduction of hazardous emissions from the process.

Search Terms: Waste Tires, pyrolysis, ASPEN Plus, exergy analysis, life cycle assessment, SimaPro.

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Abbreviations

PASH	Polycyclic aromatic sulfur hydrocarbons
FBR	Fixed bed reactors
WT	Waste tires
ZSM-5	Zeolite socony mobil -5
WLO	Waste lubricant oil
GCV	Gross calorific value
LCA	Life cycle assessment
PM10	Particulate matter with diameter of 10 micrometers
HFO	Heavy fuel oil
GWP	Global warming potential
PO	Pyrolytic oil
NCG	Non-condensable gases

Chapter 1: Introduction

1.1 Background

Nowadays, the energy demand and environmental degradation, which are due to growing population and rapid industrialization, are of top concern [1]. Initiatives are being taken to overcome the fossil fuel crisis by looking for alternatives to replace gasoline and diesel fuel. Millions of dollars are being invested in the search for alternative fuels. Meanwhile, the disposal of waste tires from automotive vehicles is becoming increasingly complex [2].

Scrap tire is considered to be a very common and significant solid waste and its production is increasing due to the increasing number of vehicles in both developed and underdeveloped countries [1].

It is reported that around 1.5 billion tires per year are produced worldwide which will eventually end-up as waste. Waste tires represent a significant proportion of the total solid waste stream. For example, approximately 3.3 million tons of waste tires were generated annually within Europe in 2010 and an estimated stockpile of 5.7 million tons of waste tires throughout Europe will be generated in the future [3].

Conversion of waste-to-energy aims to replace conventional fuels. Fuels like alcohol, biodiesel, and liquid fuel from plastics are alternative fuels for internal combustion engines. In order to prevent waste rubber from damaging the environment, it is highly desirable to recycle this material to obtain energy [2].

Currently, most waste tires are disposed of by landfilling or stockpiling, which occupies our valuable land spaces. These disposing methods, such as landfills, reusing, and burning, can create serious hazards, especially in terms of human and environmental health [1]. Only a small percentage of waste tires go into reuse/recycle options, such as being used as filler in asphalt road roadways or as a raw material for the production of secondary products, such as reclaim rubber, artificial reefs, or breakwaters.

Hence, waste tires can be considered as an energy resource [4]. It has a higher heating value, higher volatile content and lower ash content than coal and biomass. Therefore, scrap tire is a good candidate for thermal disposal application [5]. These properties make it an ideal material for thermal processes like pyrolysis and gasification [6].

A typical tire may contain up to 30 different types of synthetic rubber, 8 different natural rubbers, in addition to a range of different carbon black fillers and up to 40 different additive chemicals. The main rubber types used are, typically, styrene–butadiene-rubber, natural rubber (poly-isoprene), and poly-butadiene rubber [3]. Apart from energy and carbon material production, a wide range of materials which are illustrated in Table 1 can be recovered.

Table 1 Typical composition of vehicle and truck tires [7]

Component	Vehicle tire (wt. %)	Truck tire (wt. %)	Comments
Rubber	47	45	e.g. styrene, butadiene rubber, natural rubber and nitrile rubber
Carbon black	21.5	22	Used to strengthen the rubber and aid abrasion resistance
Metal	16.5	21.5	Steal belts and cord for strength
Textile	5.5	-	Used for reinforcement
Zinc oxide	1	2	Used (with stearic acid) to control vulcanization process and to enhance the physical properties of the rubber
Sulfur	1	1	Used to cross link the polymer chains within the rubber and also to harden and prevent excessive deformation at elevated temp.
Additives	7.5	5	e.g. Clay or silica used to partial replacement of carbon black

Researchers concluded that yields of oil, gas, and char were not significantly influenced by the type and origin of the tire. However, there were noticeable differences in the composition of the derived gases and oils [3].

Tires are manufactured to be extremely resistant to physical, chemical and biological effects which make it very difficult to apply techniques for their recycling and/or further processing. Moreover, storing represents a high risk of fire that would have serious environmental effects on the atmosphere, soil and groundwater. At present, there are a few alternatives for waste tire valorization, such as pyrolysis, gasification, and combustion [8].

Incineration/combustion, co-combustion with coal or other fuels, pyrolysis, and gasification are all considered to be attractive methods for recovering energy from waste tires. Incineration is the direct combustion of the tire and it is very common in cement kilns. Pyrolysis is the thermal degradation of organic waste in the absence of oxygen or in partial oxygen combustion conditions to produce a carbonaceous char, liquids, and gaseous hydrocarbons. Gasification refers to pyrolysis followed by higher temperature reactions of the char, tars, and primary gases with air, oxygen, or steam to yield mainly low-molecular-weight gaseous products [4]. Compared to pyrolysis and gasification, incineration products have more hazardous emissions and harmful process residues [9].

In addition, pyrolysis and gasification are conducted under less drastic conditions in comparison with classic direct combustion, resulting in reduced gaseous emissions of heavy metals. Moreover, they allow better recovery efficiency since the process by-products can be used as fuels (gas, oils), for both conventional (classic engines and heaters) and high efficiency apparatuses (gas turbines and fuel cells), or alternatively as chemical sources or as raw materials for other processes [10].

Pyrolysis of waste tire is considered to be a promising process due to the possibility for optimizing the process conditions to produce high energy density liquids, char, and gas. In addition, the liquid products can be easily stored until transported to an area where they can be most efficiently utilized [11].

However, waste tire pyrolysis oil contains impurities such as char, sand and alkali metals which will affect the performance of engines. In addition, exhaust emissions may be impaired by these impurities. It also contains tar and polymers in the form of gummy materials which may cause the formation of deposits in the injection system [12].

Compared to other petroleum products, like Diesel, waste tire pyrolysis oil has higher viscosity, sulfur contents [13] and polycyclic aromatic sulfur hydrocarbons (PASH), which are carcinogenic and mutagenic and also cause the production of toxic and corrosive SOx in the exhaust gas during combustion. Thus, one drawback is that using waste tire pyrolysis oil in a combustion engine requiring first a desulfurization process to upgrade the pyrolysis oil derived from waste tire as a an alternative fuel [14].

1.2 Literature Review

1.2.1 Pyrolysis. Pyrolysis is an endothermic process, an environmentally attractive method for the treatment of tire wastes. The process uses medium temperatures $(300 - 700)^{o}C$ and an oxygen-free environment to decompose solid tire wastes chemically in to char, oil, and gas as illustrated in Figure 1, thus producing minimal emissions of nitrogen oxide and sulfur oxide compared to incineration, the most common process in the industry. It is defined as the sum of a series of parallel and subsequent reactions that take place in the pyrolysis reactor [15]. The products obtained with this process can be easily handled, stored, and transported which increases the applicability of this method [16].
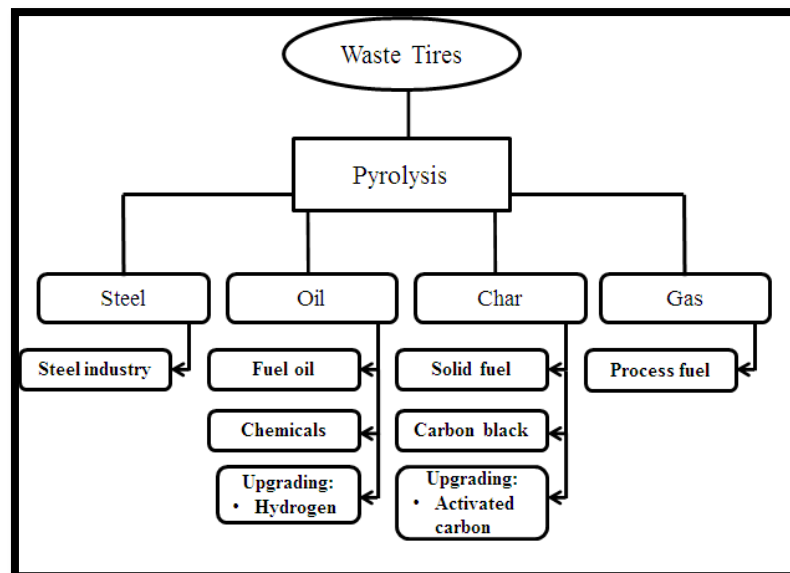
Figure 1 Pyrolysis process [3]

1.2.2 Pyrolysis types and reactor configuration. There are many classifications of types of pyrolysis depending on the operating conditions, such as the heating rate, temperature, and the gases residence time. In general, pyrolysis is classified as either fast or slow. Regarding the environment used in the process, it can be classified as oxidative pyrolysis, steam pyrolysis, hydro pyrolysis, catalytic pyrolysis and vacuum pyrolysis, and also depending on the heater system as the microwave or plasma pyrolysis. Conventionally, fluidized and entrained bed reactors are associated with fast pyrolysis whilst fixed bed reactors (FBR) are associated with slow pyrolysis (a batch or semi-batch process).

Other types of reactors such as the rotating cone (usually used for liquid production since the heating rate is high and the vapor residence time is relative short), may also be categorized as carrying out fast pyrolysis [17].

1.2.2.1 Slow pyrolysis. This type of pyrolysis, as the name suggests, considers a slow thermal decomposition at low temperatures. It is characterized by low heating rates, relatively long solid and vapor residence times, and sometimes by low temperature. Longer residence times result in leading secondary conversion of primary products, yielding more coke, tar, as well as thermally- stable products. This fact is why slow pyrolysis is sometimes referred to as carbonization. Unlike fast pyrolysis, the objective of slow pyrolysis is the char production, although tar and gases are also obtained but not necessarily recovered [17].

1.2.2.2 Fast pyrolysis. In contrast to slow pyrolysis, fast pyrolysis indicates a rapid thermal decomposition characterized by higher heating rates. This process usually requires a feedstock with small particle sizes and specially-designed devices to allow quick removal of the vapors released. Fast pyrolysis is recognized as an effective conversion route for the production of liquid fuels, chemicals and derived products with higher yield (usually around 50–60 wt. % for rubber feedstock) [17].

1.2.2.3 Rotary kiln pyrolysis. A rotary kiln is basically a rotating inclined cylinder as illustrated in Figure 2. Solid retention time in a kiln is an important design factor and is set by proper selection of the diameter, length, speed, and slope of the internal design. Most important, for the required chemical reaction(s) to take place, solids must be heated to a specific point. There are two basic types of rotary kilns; direct fired and indirect [18]. Rotary kiln reactors are the most common reactor used for pyrolysis in the industry.
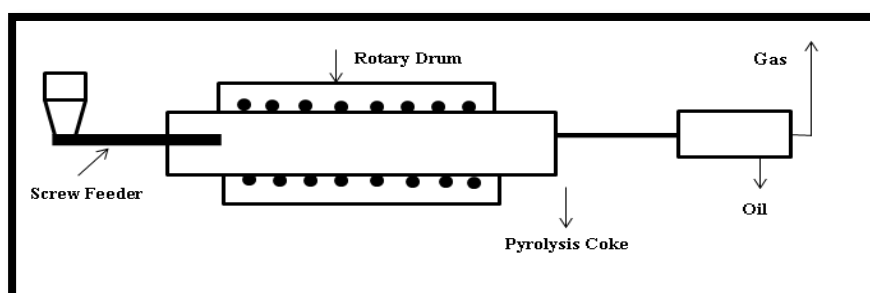
Figure 2 Rotary kiln reactor [19]

1.2.2.4 Fixed bed pyrolysis. Fixed bed pyrolysis reactors are mostly used by researchers in laboratory experiments because they are easy to construct and operate. The majorities of reactors are made of stainless steel or quartz and glass [18]. The major drawback of fixed bed pyrolysis is the poor heat transfer to large volume of tires. Thus, shredding of tires to small particles is needed. Figure 3 shows the reactor configuration.
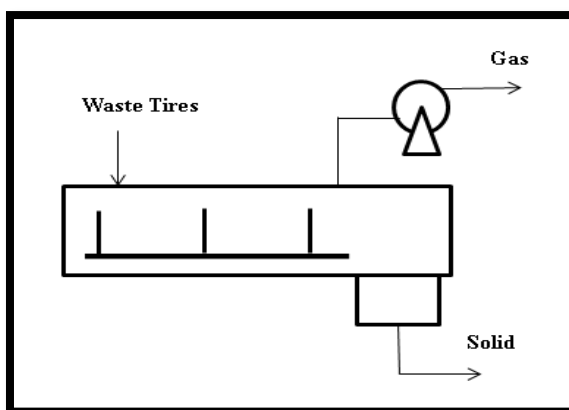
Figure 3 Fixed bed pyrolysis reactor [20]

1.2.2.5 Fluidized bed pyrolysis. Studies regarding fluidized beds are limited due to the difficulty of their operation. Figure 4 shows the reactor configuration. However, fluidized bed reactors are advantageous due to their: long residence time which contributes to secondary reactions and lower temperature and heating rate that favor carbonization which reduces oil yield (perfect if the product targeted is the gas). Pyrolysis in a fluidized bed is characterized as fast pyrolysis directly producing a liquid fuel, which is beneficial when tire resources are remote from where the energy is required, since the liquid can be readily stored and transported [18].
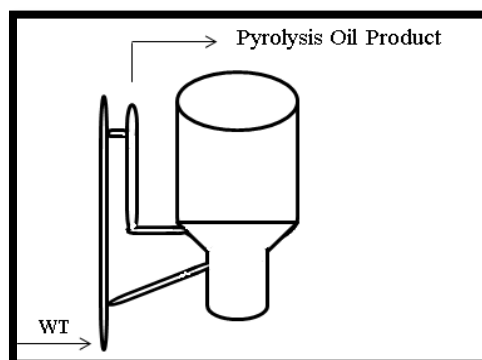
Figure 4 Fluidized bed pyrolysis reactor [21]

1.2.2.6 Ablative reactor pyrolysis. Compared to other types, ablative pyrolysis is not common. It is defined as the phenomenon occurring when a solid, exposed to high external heat flux density producing solids, liquids and/or gases can be rapidly and continuously removed from the reactor. Ablation can be exploited for carrying out the fast pyrolysis of materials such as tires. Tires are pressed against a hot surface (contact ablative pyrolysis) or intercept a concentrated radiation (radiant ablative pyrolysis) [18].

1.2.2.7 Flash pyrolysis. Flash pyrolysis is characterized by high heating rates, temperatures between 450°C to 600°C and short residence times of less than one second which make these conditions perfect to prevent cracking of the gases into non-condensable gases, maximizing the liquid product yield [18]. Figure 5 shows the flash pyrolysis reactor.
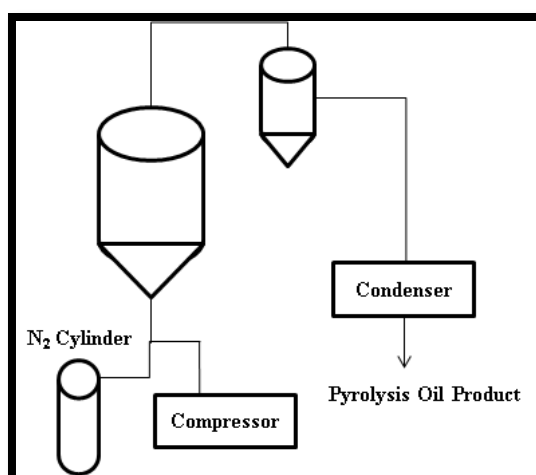
Figure 5 Flash pyrolysis reactor [22]

1.2.2.8 Catalytic pyrolysis. Catalytic pyrolysis is becoming an important area of recent investigation and is considered a very promising field. The influence of the catalyst is to reduce the yield of oil with a consequent increase in the gas yield. Thus, the catalyst causes an increase in the cracking of hydrocarbons into shorter chain lengths, which decreases oil yield while increasing the amount of gases evolved [23]. The most used catalysts are Y-type zeolite, ZSM-5, and Al2O3. In addition, single ring aromatic hydrocarbons, benzene, toluene and xylenes present in the oils, can noticeably increase in the presence of the catalyst. Naphthalene and alkylated naphthalene show a similar increase in concentration when a catalyst is present [18].

1.2.2.9 Steam pyrolysis. Steam pyrolysis of tires for oil production was also investigated by some researchers. One of the advantages of steam pyrolysis is the reduction of pyrolysis temperatures needed by up to 150°C, compared with steam-free pyrolysis. This is due to the ability of steam to diffuse into the tires and release pores and displace volatiles. Moreover, the steam reduces the partial pressures of pyrolysis gases through dilution and improves the concentration gradient flow from the tires. Therefore, the mass transfer of gases from the tires is improved during the process [23].

1.2.2.10 Plasma pyrolysis. Thermal plasma pyrolysis defined as a solid reaction with limited oxygen and high temperatures to produce gaseous and solid products. When tire particles are placed in plasma, the volatile matter is released and cracked, raising the amount of hydrogen and light hydrocarbons such as methane and acetylene. There are four main stages of plasma pyrolysis : extremely fast particle heating originating from plasma jets, a massive release of volatile matter from tire particles, very fast gasification of the homogenous phase, and finally, rapid heating and mass exchange. There are many advantages of plasma pyrolysis such as its high heating transfer rate, the desired properties of pyrolysis products, and the high possibility of eliminating dangerous substances. However, a plasma pyrolysis reactor requires a high amount of energy to achieve the required conditions. There are two major products from plasma pyrolysis: gas and solid (char) [18].

1.2.2.11 Molten salt pyrolysis. Molten-salt destruction is an alternative pyrolysis method. In this process, a molten and turbulent bed of salt is used, such as sodium carbonate, to destroy hazardous materials. Shredded solid waste is injected with air under the surface of the molten salt. Hot gases (carbon dioxide, steam, and unreacted air) rise through the molten salt bath, and pass through a secondary reaction zone and through an off-gas cleanup system before discharging to the atmosphere. The remaining pyrolysis by-products; react with the alkaline molten salt forming inorganic products that are retained in the melt. Spent molten salt containing ash; is drawn away from the reactor, cooled, and placed in landfills [18].

1.2.2.12 Microwave pyrolysis. Microwave pyrolysis involves uniform and rapid thermal energy being applied to the waste tires. This process has a high heating efficiency and short reaction time. Thus, polymers like waste tires can be easily

heated regardless of their low thermal conductivity. However, any type of rubber used in the microwave process must be sufficiently polar in structure so that the microwave energy can be absorbed at the appropriate rate to make de-vulcanization viable [18].

1.2.2.13 Co-pyrolysis. Vehicle and truck tires with waste lubricant oil (WLO) are co-pyrolyzed in a fixed bed reactor at temperatures from 550 to 800°C. Co-pyrolysis with WLO produces more oil than pyrolysis of tires alone. However, co-pyrolysis of car tires with WLO produces less liquid than co-pyrolysis of truck tires with WLO. Although the addition of WLO does not enhance the degradation of tires during pyrolysis, co-pyrolysis oils consist of higher amount of lighter fraction than commercial diesel. That means; the addition of scrap tires into WLO increases the degradation of heavy fractions in WLO [23].

1.2.3 Waste tire pyrolysis advantages and disadvantages. Pyrolysis is considered to be the most attractive processes compared to other thermochemical processes due to its minor environmental impact and the recovery of solid and liquid material. In addition, pyrolysis products are easy to manage, store, transport, and then upgrade according to different objectives. Thus, the liquid product does not have to be used at or near the recycling plant. Moreover, pyrolysis has the advantage of allowing the separation of most impurities such as sulfur from fuels prior to their combustion. Pyrolysis has minimal air pollution impacts because most of the pyrolytic gas generated is burned as fuel in the process. However, although pyrolysis of waste tires has been widely established all over the world, it is currently used to a limited extent and mainly for research purposes. One remarkable problem consists of transferring the heat efficiently to drive the pyrolysis process in such a way that the temperature is evenly distributed. This is a significant dilemma for industrial plants which discourages the promotion and economic and technical feasibility of this process. Moreover, the products from tire pyrolysis are more complex from the physical-chemical point of view compared to products from other thermochemical processes such as combustion or gasification [17].

1.2.4 Pyrolysis products. Three main products are obtained from the pyrolysis of waste tires: solid (char), liquid, and gas. The pyrolysis liquids, which are oily organic compounds, have a dark-brown color with a strong smell. Careful handling of the liquid is required since it irritates human skin. Tire pyrolysis liquid

consists of paraffins, olefins, and aromatic compounds as illustrated in Table 2. Also, It has a high gross calorific value (GCV) of around 41–44 MJ/ kg. This makes it very attractive as an alternative for fossil liquid fuels. In addition to their use as fuels, the liquids are a potential source of light aromatics such as benzene, toluene and xylene which command a higher market value than crude oils. Another important product is limonene which has extremely fast growing and wide industrial applications including formulation of industrial solvents, resins, and adhesives.

Table 2 Waste tires pyrolysis oil components [3]

Aliphatic compounds	Single ring aromatic compounds	Polyarmatic hydrocarbons (PHC)	Others
Alkanes	Toluene	Naphthalene	Hydrocarbons
Decane(C10)	Ethyl benzene	Methylnaphthalene	Limonene
Undecane(C11)	Styrene	Biphenyl	Pinene
Dodecane(C12)	Xylene(1,2-dimethyl benzene)	Ethylnaphthalene	Cyclopentene, Pentyl-Cyclohexene
Tridecane (C13)	Xylene(1,3-dimethyl benzene)	Dimethylbiphenyl	Cyclohexene, PentylCyclohexane, ethyl-Methyl-Cyclopentane, Ethylidene-Phenol
Tetradecane (C14)	Xylene(1,4-dimethyl benzene)	Dimethylnaphthalene	Methylphenol
Pentadecane (C15)	Toluene, ethyl	Acenaphthene	Dimethylphenol
Hexadecane (C16)	Benzene, propyl-	Trimethylnaphthalene	Isopropylphenol
Heptadecane (C17)	Methylstyrene	Dihydromethylnaphthalene	Phenol
Octadecane (C18)	Indene	Tetrahydronaphthalene	Methylphenol
Nonadecane (C19)	Benzene, butyl-	Fluorene	Dimethylphenol
Eicosane (C20)	Benzene, dimethyl propyl-	Methylfluorene	Isopropylphenol
Heneicosane (C21)	Benzene, dimethyl-	Phenanthrene	Methylbenzaldehyde
Docosane (C22)	Benzene, butenyl-	Anthracene	Tetradecanoic acid, Pentadecanoic acid, Hexadecanoic acid,
Tricosane (C23)	Benzene, pentyl-, Benzene, cyclopentyl-	Dimethylfluorene	Heptadecanoic acid, Octadecanoic acid
Tetracosane (C24)	Benzene, cyclohexyl-, Benzene, hexyl-	Methylphenanthrene, Methylanthracene	Sulphur compounds, Nitrogen compounds
Pentacosane (C25)	Benzene, methyl	Dimethlyphenanthrene	Aniline,Benzothiazole
(C26)–(C35)	Methylindene	Fluoranthene, Pyrene	Thiophene

Char produced from pyrolysis can be used as a solid fuel or as a raw material for activated carbon manufacture. Pyrolysis gas contains high concentrations of hydrogen, carbon dioxide, carbon monoxide, methane, ethane, propane, butadiene, and other hydrocarbon gases with a GCV of approximately 37 MJ/m^3 which is enough to provide the energy required by the pyrolysis process [11].

The utilization of tire pyrolysis oil as an alternative fuel for diesel engines can minimize the usage of natural sources however; it contains tar and polymers in the form of gummy materials which may cause the formation of deposits in the injection system. In addition, it may block the combustion chamber, exhaust valves, and the piston ring grooves [12]. Moreover, as illustrated in Table 3 and 4, compared with petroleum products it has a higher viscosity and sulfur content [13].

In addition, pyrolysis oil presents a wide distillation range with significant contents of olefinic and aromatic compounds that limit its direct use in internal combustion engines as; these characteristics give way to both a lower flash point and cetane number than standard diesel fuels. Conventional diesel fuels have a cetane number between 40 and 55 while waste tire oil has values between 40 and 44 which mean that the fuel will have a long ignition delay and therefore more fuel is used before the first fuel particles ignite. This results in a poor thermal efficiency and a rough running engine in addition to undesirable levels of exhaust smoke and emissions [17].

Thus, for internal combustion engine applications, pyrolysis oil needs upgrading to be used as a substitute to fossil diesel without any significant modifications to the engine. Some of the important desired properties are: low solid content, good homogeneity and sufficiently high flash point [24].

Engine performance can be improved and emissions can be reduced by further processing of pyrolysis oil through sulfur reduction, moisture removal, and distillation [1].

1.2.5 Exergy analysis. Many thermodynamic systems can be treated as being in stable equilibrium but not in equilibrium with the surroundings. Any system not in the same temperature as the environment is considered to be not in a mutual stable equilibrium [25].

Table 3 Fuel properties of waste tire pyrolysis oil

Property	Ref. [26]	Ref. [27]	Ref. [28]	Ref. [29]	Ref. [30]
Flash Point (^{o}C)	20	17.5	43	65	32
Carbon residue (%)	2.2	1.78	-	-	-
Density (kg L^{-1})	0.91	0.962	0.924	0.833	0.957
Viscosity cSt (at 40 ^{o}C)	6.30	-	3.77	-	-
Viscosity cSt (at 50 ^{o}C)	-	2.44	0.924	1.01	-
Viscosity cSt (at 60 ^{o}C)	2.38	-	-	-	-
Carbon (wt.%)	88.0	84.26	-	79.61	85.86
Hydrogen (wt.%)	9.4	10.39	-	10.04	9.15
Nitrogen (wt.%)	0.45	0.42	-	0.94	0.65
Sulfur (wt.%)	1.5	1.54	0.72	0.11	1.25
Oxygen (wt.%)	0.5	3.39	9.3	-	2.87
Initial B.Pt. (^{o}C)	100	-	70	38.5	-
10% B.Pt. (^{o}C)	140	-	114.5	58.2	-
50% B.Pt. (^{o}C)	264	-	296.1	174.8	-
90% B.Pt. (^{o}C)	355	-	386.4	-	-
Calorific value (MJ kg^{-1})	42.0	41.7	38.0	42.66	42
Ash (%)	0.002	Trace	0.31	-	0.22
Moisture (vol. %)	4.6	0.88 (wt. %)	-	-	

Table 4 Properties of diesel fuel [31]

Property	Diesel Oil
Specific gravity,15/15 ^{o}C	0.8426
API gravity	36.43
Water content vol. %	Nil
Ash content wt. %	0.0247
Aniline point, ^{o}C	78
Diesel index	62.8
Cetane index	53.9
Calorific value, MJ/kg	46
Flash point, ^{o}C	85
Sulfur content (wt. %)	0.041

Exergy is defined as the maximum work that can be obtained from a system. It is conserved when the system processes and the surroundings are reversible and destroyed when any irreversible process appears [32].

Exergy analysis is the process of evaluating the maximum work that can be extracted from a system with respect to a reference state [33]. In order to evaluate the extractable work from a process it is necessary to compare it with an arbitrary reference state.

1.2.5.1 Exergy aspects. It is important to illustrate some exergy characteristics:

- Any system in stable equilibrium with the environment; no difference in temperature, pressures and concentrations have zero exergy.
- The exergy of a system increases as the system deviates from the environment.
- Exergy is a measure of the useful energy of a system which mean, when energy quality decrease more exergy is being destroyed.
- By definition, exergy depends on both system and environment states.
- Exergy efficiency is a measure of system reversibility or ideality.

1.2.6 Exergy balance. The concept of exergy can be introduced by using reversible work. Exergy balance is a combination of energy and entropy balance equations of a certain control volume [34].
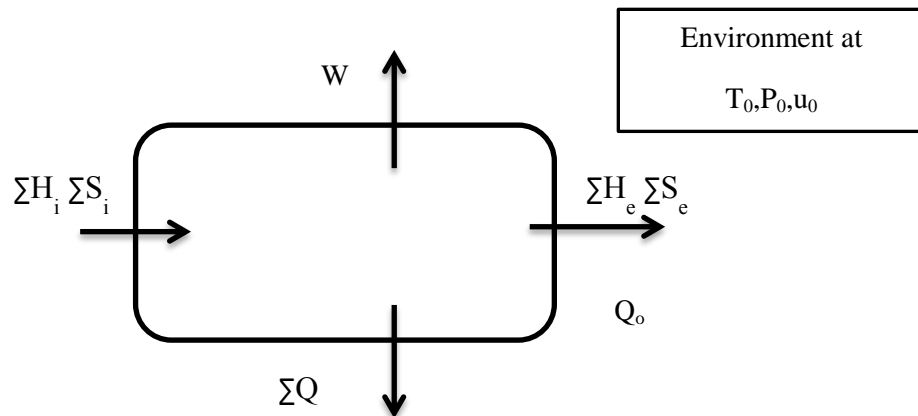
Figure 6 Control volume with inlet and outlet streams

By conducting energy and entropy balance for the system illustrated in figure 6, the following equations will result:

$$\sum Q - \sum H_e - \sum H_i + W \qquad \text{Eq. (1.1)}$$

where Q is the heat added or extracted from the system, H_i and H_e are the inlet and outlet streams enthalpies and W is the work done by or on the system.

$$\sum s_e - \sum s_i - \int_{T_i}^{T_e} \frac{\delta Q}{T} + s_{gen} \qquad \text{Eq. (1.2)}$$

where s_e and s_i are the outlet and inlet streams entropies and s_{gen} is entropy generated during a process.

The maximum work can be calculated by introducing a Carnot engine to the control volume, where Q_o is the rejected heat from the engine. The energy and entropy balance equations will be:

$$Q_o - \sum H_e - \sum H_i + W_{max} \qquad \text{Eq. (1.3)}$$

where Q_o is the surrounding energy or heat and W_{max} is the maximum work obtained by or on a system.

$$\sum s_e - \sum s_i - \frac{Q_o}{T_o} \qquad \text{Eq. (1.4)}$$

where T_o is the environment temperature. The exergy balance equation can be obtained by combining the entropy and energy equations as:

$$[H_i - H_e - T_o(s_i - s_e)] = W + Q\left[1 - \frac{T_o}{Q}\int_{T_o}^{T_e}\left(\frac{\delta Q}{T}\right)\right] + T_o s_{gen} \qquad \text{Eq. (1.5)}$$

When all the processes inside the control volume are reversible, the control volume reaches a stable equilibrium with the surroundings which means that the outlet streams are in equilibrium with the environment. Eq. (1.5) can be written with respect to maximum work as:

$$[H_i - H_e - T_o(s_i - s_e)] = W + Q\left[1 - \frac{T_o}{Q}\int_{T_o}^{T_e}\left(\frac{\delta Q}{T}\right)\right] - W_{max} \qquad \text{Eq. (1.6)}$$

For rotary kilns or any energy conversion process, the exergy balance equation can also represented by using exergy values of inlet and outlet streams of the process [35]:

$$\sum_{in} Ex_j = \sum_{out} Ex_k + I \qquad \text{Eq. (1.7)}$$

where $\sum_{in} Ex_j$ and $\sum_{out} Ex_{jk}$ are the sums of inlet and outlet streams exergies respectively. I is the irreversibility or internal exergy loss (available work) generated from the loss of material and energy qualities due to dissipation [36].

Exergy for a stream depends on its material composition which is represented by chemical exergy $EX_{ch,i}$ and on its pressure and temperature represented by physical exergy $EX_{ph,i}$ [35]:

$$EX_i = EX_{ch,i} + EX_{ph,i} = m_i(e_{ch,i} + e_{ph,i}) \qquad \text{Eq. (1.8)}$$

where $e_{ch,i}$ and $e_{ph,i}$ are the specific chemical and physical exergy of a pure component i.

Physical exergy of pure component i is represented by:

$$e_{ph,i} = (h - h_0)_i - T_0(s - s_0)_i \qquad \text{Eq. (1.9)}$$

where h and s are the stream enthalpies and entropies at a specific temperature and pressure. h_0 and s_0 are the enthalpy and entropy at the surrounding temperature and pressure.

For ideal gases, with known heat capacity cp, the physical exergy can be calculated by the following equation:

$$e_{ph,i} = \int_{T_0}^{T} cp_{,i}(T)dT - T_0 \int_{T_0}^{T} \frac{cp_{,i}(T)}{T} dT + RT_0 \int_{P_0}^{P} dp \qquad \text{Eq. (1.10)}$$

For liquids and solids, where the heat capacity c and the average specific volume v_m between P and P_0 are assumed to be constant, the expression of the physical exergy can be:

$$e_{ph,i} = c \left[(T - T_0) - T_0 \ln(\frac{T}{T_0})\right] + v_m(P - P_0) \qquad \text{Eq. (1.11)}$$

The chemical exergy of a gaseous stream is represented by the following equation:

$$e_{ch,i} = \sum_i y_i e_{ch,i}^0 + RT_0 \sum_i y_i \ln y_i \qquad \text{Eq. (1.12)}$$

where y_i is the composition of component i in the stream, $e_{ch,i}^0$ is the standard chemical exergy of a pure component which represents the maximum work when a component is brought from environmental state T_0 and P_0 [37].

The chemical exergy for non-conventional materials can be calculated using the Szargut and Styrylska correlation [38]:

$$e_{ch,s} = LHV.\left(1.0401 + 0.1728\frac{x_H}{x_c} + 0.0432\frac{x_o}{x_c}\right.$$
$$\left. + 0.2169\frac{x_s}{x_c}\left(1 - 2.0628\frac{x_H}{x_c}\right)\right) \qquad \text{Eq.}(1.13)$$

where *LHV* is the lower heating value of the material and x_c, x_H, x_s, and x_o are the elements in the material mass fractions.

Another method to calculate the chemical exergyis by using Gibbs energy of formation and any reaction that include the material that chemical exergy is needed to be calculated for.

$$e_{ch} = -\Delta G + \left[\sum_{Prod} n * e_{ch} - \sum_{React} n * e_{ch}\right] \qquad \text{Eq.}(1.14)$$

where *n* is the number of moles of each product and reactant and *ΔG* is the Gibbs free energy.

There are many expressions to represent exergy efficiency. The most common expressions are general exergy efficiency and useful exergy efficiency. They are used to analyze the overall performance of thermal engines and chemical processes [39].

The general exergy efficiency of a system *ψ* is the ratio between the outlet and inlet streams' exergies [40]:

$$\psi = \frac{\sum_{out} Ex_k}{\sum_{in} Ex_j} \qquad \text{Eq.}(1.15)$$

The useful exergy efficiency is defined as the ratio of the useful outlet exergy to the total inlet exergy:

$$\psi_k = \frac{Ex_{product}}{\sum_{in} Ex_j} \qquad \text{Eq.}(1.16)$$

1.2.7 Previous exergic analysis of pyrolysis process efforts. There are many studies of exergy analysis for thermal conversion processes such as gasification, pyrolysis, and incineration have been conducted; however, only a few studies were done for pyrolysis.

One of the studies that considered pyrolysis exergy analysis is by Peters et al. [41] who studied the exergetic analysis of a fast pyrolysis plant producing crude bio-oil from lignocellulosic feedstock. Boateng et al. [42] also conducted an exergy balance of a fast pyrolysis process; theirs looked at a bench-scale plant producing bio-fuel from commodity crops. Medina et al. [43] evaluated the pyrolysis of dichrostachys cinerea in a fixed bed reactor using exergy analysis. Wang et al. [44] established an exergy model to evaluate the exergy assessment and energy consumption of a coal pyrolysis process. Tanaka et al. [45] studied the exergy analysis of different waste-to-energy systems such as high pressure boilers and waste pyrolysis – gasification systems.

1.2.8 Life cycle assessment. As part of environmental issues that are being addressed by industry, political bodies and public opinion, life cycle assessment become an interesting field that deals with the effect of the whole product system.

Life cycle assessment is the process of following the product from the cradle, where the raw materials are extracted from natural resources, then on to production and use and finally the grave where waste is disposed [46]. It evaluates the natural resource use and pollutant emissions to the environment. To conduct an LCA study, a lot of environmental information needs to be collected and analyzed in order to be able to understand the effect of a product on the environment.

There are many applications of LCA: decision making, studying process improvement possibilities, and understanding the environmental properties of a product and the relationships of the production system [47]. LCA has a series of international standards (i.e. ISO 14040-14043); which issued in 1997.

1.2.9 LCA methodology. There are four main phases of an LCA procedure: goal and scope definition, inventory analysis, impact assessment, and result interpretation.

1.2.9.1 Goal and scope definition. In order to define the goal of LCA, certain questions need to be answered [48]:

- What is the process or product to be studied?
- Why does the process or the product need to be studied?

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- Who is the targeted audience?
- Are the results for comparative assertions or to be released to the public?

LCA is usually used to compare two or more options and evaluate the advantages and disadvantages of the options under study. Also, LCA is performed to qualify and quantify the environmental impact of a specific process or product.

An LCA's scope definition requires identifying what is included and excluded from the study and the parameters of the analysis as illustrated in Figure 7. ISO standards have specific points which must be included in the scope definition stage [48]:

- Establish the product unit of analysis (functional unit) and its performance.
- Identify the system boundary and allocation options: what is included in and excluded from the study and dividing loads with respect to products.
- Include the impact assessment choices and interpretation methods
- Identify data sources and data quality requirements
- Identify types of environmental impacts to be studied

Defining the product to be analyzed is an essential step in scope definition, especially when comparing different options. Typically, a functional unit of the product needs to be identified. A functional unit is the unit of study that includes quality, quantity and duration of the service or product under analysis.

Defining the system boundary is also an important step in the scope phase, in which the natural and industrial processes to be included or excluded are decided, which process inputs and outputs to study, and which environmental impacts will be evaluated.

Multifunctional processes need to be treated carefully; as the processes produce many products and some of them depend on the production of another product. Two models were developed in LCA to deal with multifunctional processes [49]:

- Consequential model or system expansion: this model is applied when the goal of the LCA is to study the effect of a certain change in the process on the environment.

- Attributional model or allocation: allocation is performed when the goal is to identify the environmental impact of a process or to compare the impacts of different products that have the same functional unit. There are two ways to deal with allocation: subdivide the multifunctional process into sub-processes with separate inputs and outputs or use the relationships between inputs and outputs to allocate the impacts for each product. Such relationships include physical relationships such as mass, volume, and energy.

Usually, LCA studies eliminate specific processes from the analysis such as manufacturing the fixed and mobile equipment and employee labor. The diagram of system boundary is a representation of LCA scope. The diagram should clearly identify what is included and which inputs and outputs are to be tracked during the analysis.
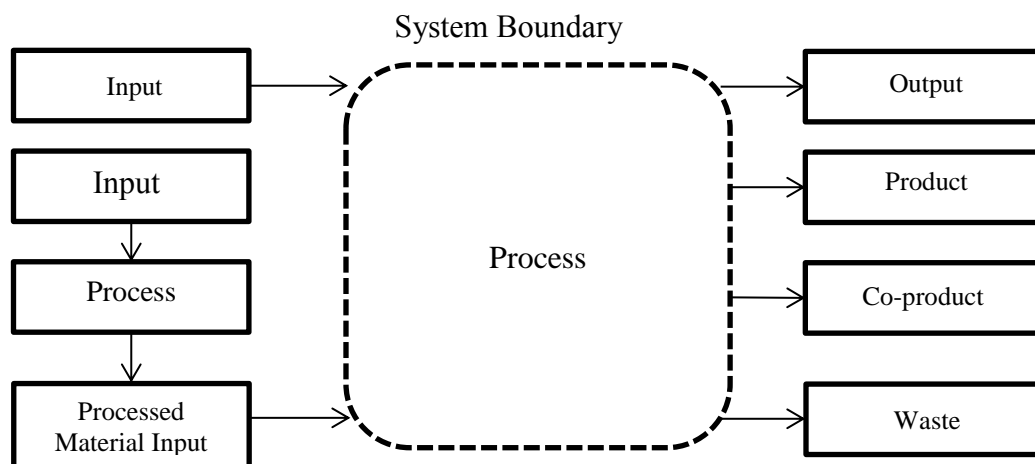
Figure 7 Process boundary [48]

There is a wide range of LCA methods that can be employed including impact assessment methods, interpretation methods, and allocation options. LCA has different environmental impact categories such as resource use, human health and ecological consequences [50]. These categories should be related to more practical classifications such as resource depletion, acidification and global warming.

Collecting inventory data depends on which impact categories were chosen because not every type of emission contributes to each type of impact.

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1.2.9.2 Inventory analysis. In the inventory analysis phase, a flow model of a technical process needs to be constructed. As illustrated in Figure 8, the model is a mass and energy balance of the system where only the flows that are environmentally relevant are considered. The models are statistic and linear which means there is no need to include time as a variable [46].

The steps of the inventory analysis are:

- Constructing the system flowchart based on the boundaries chosen in the goal and scope definition stage.
- Collecting the data for each activity in the product system then documenting the collected data.
- Calculating the environmental loads (pollutant emissions and resource use) of the system with respect to the functional unit.

In the construction of the flowchart phase, the system boundary diagram constructed in the goal and scope definition step will be elaborated to give more details. The flowcharts can be simple or complex depending on the number of the recycling loops available in the process.

The data collection step is considered as the most time consuming activity in inventory analysis. It is important to define the type of data needed to be collected such as numerical, descriptive and qualitative data. The amounts of input and output streams are considered as numerical data. Qualitative data is the information that describes the technical part of the process such as how emissions are measured and the geographical location of the system.

In the calculation of environmental loads, certain steps need to be followed:

- Relate the inputs and outputs of the process to one product, i.e. normalize the data for each activity. This step is important as the inventory data rarely fits the calculations initially.
- Use the functional unit as a reference to calculate the streams connecting the activities in the flowchart. This can be achieved by conducting a mass balance for each activity in the flow chart.
- Calculate the streams passing through the system boundary with respect to the functional unit.

- Summarize the emissions to the environment and resource use for the whole system
- Document the calculation results.

ISO 14044 standards recommend arranging the inventory data into four main categories:

- Inputs, which consist of energy and raw materials.
- Products, including co-products and waste.
- Emissions to air, soil, and water.
- Other environmental aspects.
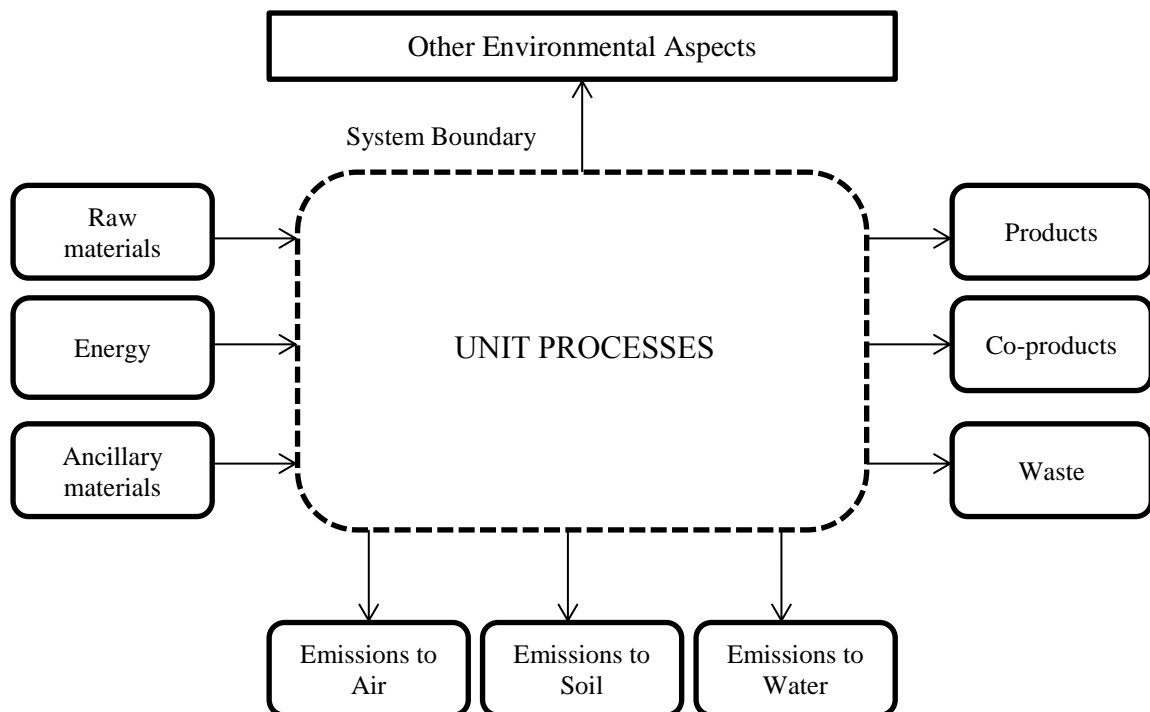
Figure 8 Classification of inventory data [48]

After collecting the data, the result of the inventory analysis is compiled in a list consisting of the total inputs from nature and the emissions to water, air and land.

1.2.9.3 Impact assessment. In the impact assessment stage, environmental emissions and resource use are related to the estimations of natural resources and the environment's impact on human health. The type of emissions may occur in the analysis depend on the system under study. In order to understand the impact of an emission, firstly, the type of environmental impacts to study must be chosen. Then, the influence of emissions on each impact must be identified and finally the total

relative impacts must be calculated [51]. The procedure order is important; i.e. identifying the environmental impacts to analyze must be done before knowing the results [52]. To translate emissions to impacts each emission must be multiplied by a characterization factor which represents the contribution of the emissions to the environmental impact. Relating an emission to an environmental impact must be done by understanding the mechanisms between impact and emission [53].

The impact assessment phase must have characterization and classification steps where which method for calculations and which environmental impacts to be use should be identified. Also, optional steps such as weighing and normalization can be included.

In the normalization step, the value of an impact indicator can be evaluated with respect to a reference where it gives an idea about whether the result is high or low based on the reference. Also, as each impact category has different units as illustrated in Table 5 and 6, normalization can be used to solve this incompatibility to be able to compare between different categories [49].

Weighing is considered the most difficult step in impact assessment because it is subjective and not based on science. In this step, the significance of each impact category must be assessed to determine the suitable weight (weighing factor).

Table 5 Common LCA environmental impacts [54]

Environmental Impact	Unit
Acidification	Kg-SO_{2e}
Eutrophication	Kg/Ne
Climate Change/Global Warming	Kg-CO_{2e}
Ozone Depletion	Kg CFC-11_e
Human Health	Varies
Photochemical Ozone Creation /Smog	Kg Ethane
Depletion of Abiotic Resources (elements)	Kg Sb_e
Depletion of Abiotic Resources (fossil)	MJ
Depletion of Non-Renewable Material Resources	MJ
Depletion of Non-Renewable Energy Resources	MJ

Table 6 Common resources used in LCA [54]

Recourse	Unit
Renewable Material Resources	MJ
Renewable Primary Energy	MJ
Freshwater Consumption	M^3 or Liters
Hazardous Waste Produced/Disposed	kg
Non-Hazardous Waste Produced/Disposed	kg
Radioactive Waste Disposed	kg
Materials for Recycling	Kg
Materials for Energy Recovery	Kg
Materials for Re-Use	Kg
Exported Energy per Energy Carrier	Kg

1.2.9.4 Result interpretation. The last step in LCA is interpretation which will be conducted after the inventory analysis and the impact assessment. There are a number of tests which need to be conducted to decide if the conclusions are consistent with the data presented in the study.

The data must be analyzed to identify the most significant issues. Three main evaluation methods must be followed [51]:

- Completeness Check: Ensure that LCA data and information is complete; i.e. no missing emissions to the environment. If there is any data missing, a new analysis is required.
- Sensitivity Check: Evaluate the sensitivity of the analysis to change. This is done by changing the assumptions or methods used to assess the validity of the final results.
- Consistency Check: Evaluate the study to check if the analysis is consistent with the established goal and scope.

Other data evaluation methods are: Result contextualizing to understand the significance, evaluating processes that contribute in selecting environmental impacts and variability quantifying of both the inventory input data and the processes under study.

After evaluating the result's significance and data assessment, limitations, conclusions and recommendations must be generated.

1.2.10 Previous life cycle assessment of pyrolysis process efforts. Many studies of life cycle assessment of pyrolysis processes have been conducted. Different studies were conducted for different raw materials. Two main paths were dominant: compressive life cycle assessment between different thermal conversion processes or qualifying the environmental impacts of different pyrolysis processes.

One of the studies that considered the LCA of pyrolysis process was done by Zhong et al. [55] who studied the LCA of flash pyrolysis of wood waste to produce bio-oil for power generation. Also, Steele et al. [56] studied the LCA of production of bio-oil by pyrolysis using wood as a raw material. Wang et al. [57] investigated if a fast pyrolysis of municipal solid waste is environmentally friendly or not and also conducted a sensitivity analysis to study the effect of bio-oil yield on global warming potential. Grierson et al. [58] studied the environmental impacts of microalgae cultivation, oil extraction, and the pyrolysis processes where the results indicated that the highest contribution on the impacts was coming from upstream processes.

Other studies focused on comparative LCA where different processes were analyzed to decide which option is preferred. Lombardi et al. [59] conducted an LCA to compare between different processes of waste tire disposal: combustion, use as heating material in the cement industry, reuse as a filling material, and a mechanical pulverization process where the most preferred option was the waste tires being used for heating in cement plants or in waste-to-energy combustion processes. Khoo [60] carried out a comparative LCA to evaluate the environmental impacts of different municipal solid waste thermal conversion processes: gasification, pyrolysis-gasification, thermal cracking gasification. The study showed that the highest environmental impacts came from gasification and thermal cracking gasification. Lettieri et al. [61] also conducted a study to compare between different municipal waste-to-energy processes (i.e. fast pyrolysis, gas plasma cleaning and gasification), where the results showed that gasification and plasma cleaning have better environmental performance than other processes.

1.3 Research Objectives

As mentioned earlier, pyrolysis of waste tires is a growing field that has the potential to replace conventional fuel production processes.

This research is aiming to give a better insight of the waste tires pyrolysis process by exploring the following aspects:

- Specify a typical pyrolysis process to analyze.
- Simulate the proposed process using a computer-aided simulation package (Aspen Plus$^®$ 8.4).
- Conduct an exergy analysis to evaluate the performance of the process
- Carry out a life cycle assessment using SimaPro 7.3.2 software to study the environmental impacts of waste tire pyrolysis.

1.4 Research Significance

Waste tire pyrolysis is considered a new field. A lot of information is missing regarding this topic. First of all, due to the complexity and danger of conducting experiments in the laboratory; simulation of the process is necessary to provide save environment and to have a better understanding of the process optimum operation conditions, products compositions, and how those conditions affect the product yield. Previous work had been done on simulation of pyrolysis process was limited on biomass pyrolysis where different products within a small range of diversity are being produced. The work conducted in this investigation is the first of its kind on the simulation of WT pyrolysis in term of considering the difficulty due to the components produced diversity. Also, the limitation of using certain models and their effect on products yield was studied.

In general, pyrolysis process is a thermal conversion process, where a considerable amount of heat will be rejected from the system. Hence, an analysis of the process thermal performance is needed which can be achieved by conducting an exergy analysis. Previous work on exergy analysis of pyrolysis process was done for different reactor configurations. However, evaluating the exergetic efficiency of the WT pyrolysis in an indirect heating rotary kiln reactor which is conducted in this investigation is very important because rotary kilns are the most common used reactors in the industry.

Moreover, WT pyrolysis is a new field especially in the Middle East and there are undiscovered aspects such as the effect of the process on the environment. The LCA study conducted in this work is essential because there is no data in literature about the effect of waste tire pyrolysis on environment worldwide. It is considered as an important contribution to the knowledge because pyrolysis process is a growing field and a lot of questions must be answered especially the environmental impacts of the process.

1.5 Research Organization

This work presents important contributions in the field of waste tire pyrolysis. The background information on the need for waste-to-energy processes, a review of different pyrolysis processes and their advantages and disadvantages, an introduction to the pyrolysis process and a literature review on exergy analysis and life cycle assessment have been presented in Chapter 1. Chapter 2 covers the process simulation using a computer aided simulation package (ASPEN Plus$^{®}$ 8.4). Chapter 3 presents the exergetic analysis for the pyrolysis process and the exergy efficiency to give an indication of the process performance. Chapter 4 presents the life cycle assessment using SimaPro 7.3.2 for the pyrolysis process to evaluate the environmental impacts of the process and a brief analysis and interpretation of the results are also presented. Finally, conclusions, recommendations for improvement, and proposed future work are presented in Chapter 5.

Chapter 2: Waste Tires Pyrolysis Process Simulation

In this chapter, an ASPEN Plus® simulation of the pyrolysis process is presented. Within the simulation, the pyrolysis reaction is carried out with basic assumptions: steady state kinetic free model, isothermal system, all sulfur represented as H_2S, and char are assumed as pure carbon to reduce complexity [62].

Pyrolysis is carried out by reacting tires in a no-oxygen environment. Heat produced from the combustion of fuel maintains the reactor temperature to carry out the endothermic reactions inside it. The pyrolysis processes can be divided into four physic-chemical processes as shown in Figure 9. The simulation is modeled for a 10 ton per day capacity of tires.

The pyrolysis reactor has been modeled in four stages. In the first stage before using the pyrolysis reactor, the moisture content of the tires is reduced by drying. In the second stage, the tires are decomposed into conventional components because tires are considered as a non-conventional material in ASPEN Plus®. In the third stage the pyrolysis reaction is conducted by minimizing the Gibbs energy [63]. The gaseous product is condensed using a water cooler to produce the pyrolytic oil. Table 7 shows the models used in the simulation.

Table 7 ASPEN Plus® unit operation model description

Aspen Plus ID	Block ID	Description
RStoic	DRYER	Moisture content of tires reduction.
RYield	DECOMP	Conversion of Non-conventional materials (Tires) to conventional components using FORTRAN statement.
RGibbs	REACT	Calculation of the product composition by minimizing Gibbs free energy.
SSplit	SEP	Separation of the gaseous products from char and ash by specifying split ratio.
Heater	CONDENSE	Condensation of the gases to produce pyrolytic oil.
Flash2	SEP2	Separation of the oil from non - condensable gases.
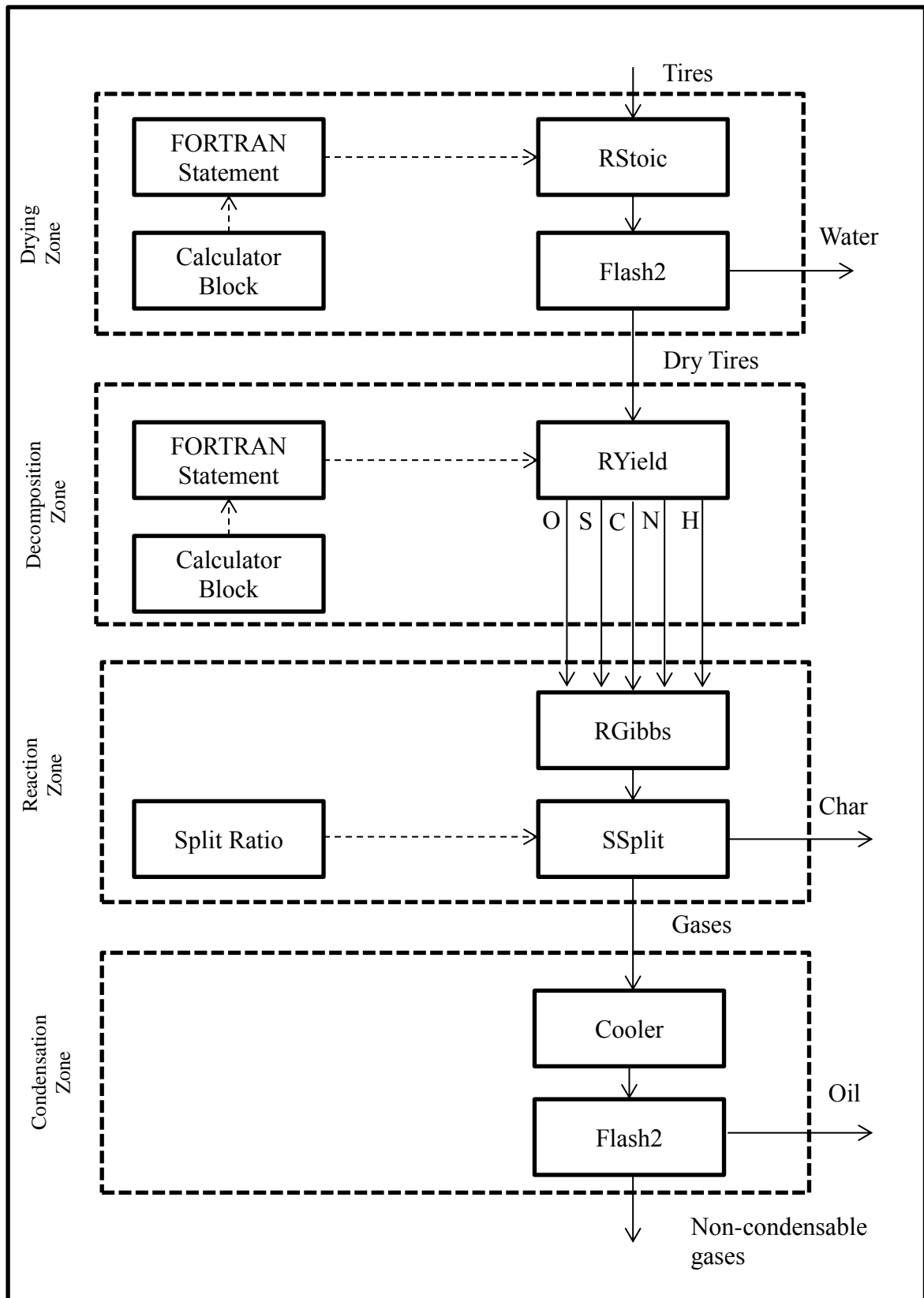
Figure 9 ASPEN Plus[®] calculation procedure

2.1 Process Discerption

2.1.1 Physical property method. In order to estimate the physical properties of the conventional components in the pyrolysis process, the Peng-Robinson with Boston-Mathias alpha function equation of state (PR-BM) was used. Alpha is a temperature dependent parameter that improves the pure component vapor pressure correlation at very high temperatures. For this reason, PR-BM is suitable for the pyrolysis process since it is carried out at relatively high temperatures. The density and enthalpy models for tires and ash are DGOALIGT and HCOALGEN.

2.1.2 Pyrolysis model description. As mentioned earlier, the pyrolysis process converts tires to oil, non-condensable gases and char byproduct. The ASPEN Plus[®] flowsheet of the process is presented in Figure 10. As illustrated in Figure 9, four blocks have been used to simulate the pyrolysis process. Tires are considered as a non-conventional material which is modeled in the simulation by using the proximate and ultimate analysis that is presented in Table 8.

Table 8 Proximate and ultimate analysis of tire [64]

Proximate Analysis	
Fixed Carbon (%w/w$_{dry}$)	33.5
Volatile (%w/w$_{dry}$)	61.3
Ash (%w/w$_{dry}$)	4.4
Moisture (%w/w$_{dry}$)	0.8
Ultimate Analysis	
N (%w/w)	0.4
C (%w/w)	85.2
H (%w/w)	7.3
S (%w/w)	2.3
Ash (%w/w)	4.4
O (%w/w)	0.4

The RStoic block (DRYER) is used to model the drying process of tires where a FORTRAN statement in the calculator block is used to control the operation. The dry tires are fed to the next stage.

The RYield block (DECOMP) is used to decompose tire (non- conventional material) into its elements (H, C, O, N, S). This step is conducted by using RYield block connected with calculations based on components yield specifications where the total yield of the volatiles is assumed to be equal to volatile content in the proximate analysis of the tires. The tires yield distribution into its elements was specified by using a FORTRAN statement in a calculator block. The statement evaluates the mass flow rate of the elements in the outlet stream from the Ryield block.

The RGibbs block (REACT) is used to model the pyrolysis of waste tires where it evaluates the chemical equilibrium composition of the product by minimizing the Gibbs free energy. The decomposed tires enter the reactor where the pyrolysis reaction takes place at $450^{o}C$ at atmospheric pressure. The products from the RGibbs reactor pass through a unit operation model SSplit (SEP) where the char is separated from the gases based on a specific split ratio.

Then, the gaseous stream leaving SSplit enters a water cooler (CONDENSE) where the gasses are condensed to form a liquid fraction. The final stage in the simulation is the Flash2 block (SEP2) where the liquid is separated from the non-condensable gases. The liquid fraction then leaves the pyrolysis plant as the pyrolytic oil product.

2.2 Results and Discussion

2.2.1 Model validation. Experimental data of the product composition from a pyrolysis process and the oil yield was used to validate the simulation model [63]. To investigate the effect of temperature on the oil yield, another study was used to validate the simulation results [11]. There is a considerable difference between the simulation results and the experimental data.

The basic process was modeled in specific operation conditions (i.e. 450 ^{o}C and atmospheric pressure with the assumption of no pressure drop).
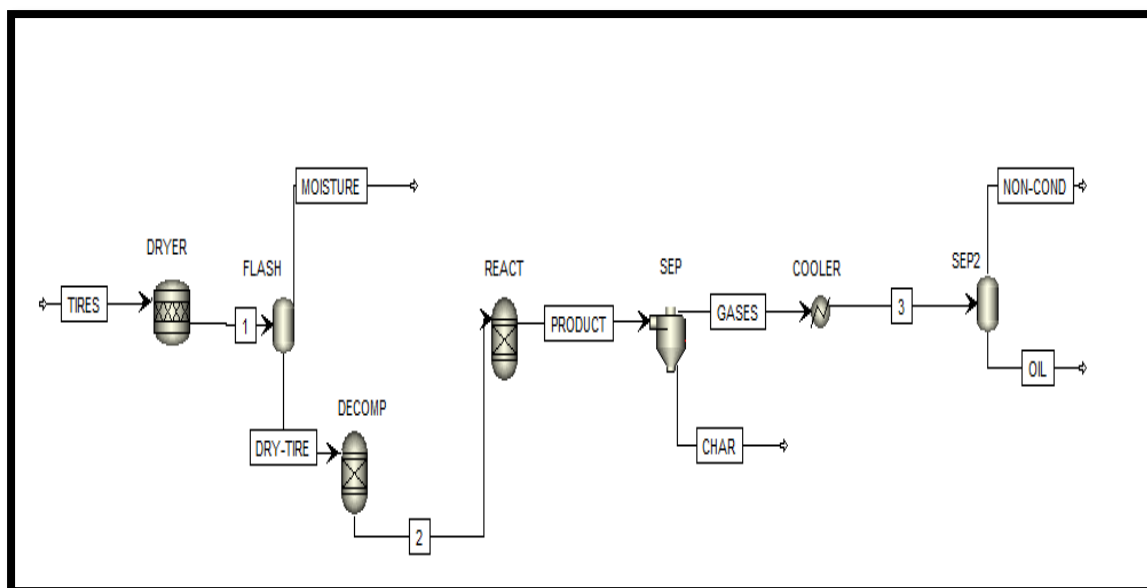
Figure 10 ASPEN Plus model of pyrolysis process

Table 9 shows the pyrolytic oil component concentrations. No errors occurred in the simulation which proves that the model is viable. Then, the effect of temperature was studied for temperatures ranging from $400 - 900\,^oC$. The results at different temperatures are presented in Appendix A.

Table 9 Composition of components produced from pyrolysis process at 450 ^oC (w/w)

Component	Simulation Model	[65]
Water	2.3E-01	-
Carbon dioxide	3.5E-02	7E-3
Carbon monoxide	4.7E-03	5.2E-2
Hydrogen sulfide	5.6E-02	-
Nitric oxide	4.27E-19	-
Nitric dioxide	6.85E-34	-
Methane	0.6619	1E-2
Ethane	2E-05	7E-3
Propane	2E-09	6E-3
Ethylene	2E-08	5E-3
Propylene	3E-11	9E-3
1-Butene	3E-15	2E-3
N-Butane	2E-13	2E-3

Table 9 (Continued)

Component	Simulation Model	[65]
Benzene	3E-16	3.2E-2
Toluene	2.64E-15	2.1E-2
Ethyl benzene	2.00E-19	1E-2
O-Xylene	5.47E-19	-
M-Xylene	1.13E-18	1.2E-2
P-Xylene	4.58E-19	1.2E-2
Styrene	3.37E-21	7E-3
Isobutylene	1E-14	5E-3
1,3-Butediene	5E-17	1E-2
Trans-2-Pentene	9E-19	Tr.
Cis-2-Butene	4E-15	Tr.
N-Pentane	2E-17	1E-3
2-Methyl-2-Butene	3E-18	Tr[*].
3-Methyl-2-Pentene	1E-21	-
2,3-Dimethyl-1-Butene	3E-22	-
Isobutane	1E-13	1E-2
Trans-2-Butene	5E-15	Tr.

*Tr. =Traces

Due to the diversity of components of pyrolytic oil, it is difficult to quantify and measure them. As illustrated in Table 9, the simulation model failed to evaluate the composition of the higher alkanes (C_{10}-C_{35}), and the concentrations of the other components (i.e. hydrocarbon gases C_1-C_5, olefins, carbon monoxide and carbon dioxide) are significantly different from the literature. The main reason for these inconsistent results with the literature is the Gibbs model used in the simulation where the product compositions were calculated by minimizing Gibbs free energy. In order to develop reliable results consistent with the literature, a kinetic reaction model based on reaction mechanisms needs to be established to predict the pyrolysis products with respect to feedstock composition and reaction operating conditions [66]. Then, the produced pyrolytic oil yield and component composition can be evaluated with a high level of detail.

2.2.2 Sensitivity Analysis. A sensitivity analysis was carried out by studying the effect of temperature on the pyrolytic oil yield and component composition. The temperature of the pyrolysis reactor (RGibbs block) was varied from 400°C to 900°C at every 50°C. The effect of temperature on the pyrolytic oil yield is represented in Figure11. As illustrated, the oil yield is not consistent with the literature as the highest yield evaluated was 7.67% at 400°C which is significantly different from other studies were the pyrolytic oil yield reaches up to 50% at the same temperature range [65] [11] [29]. At relatively low temperature (i.e. 400°C) the carbon content in tires is not converted completely, so the oil yield will be low but it will increase with increasing temperature.

Table A.1 in Appendix A shows the effect of temperature on the yields of different fractions. As illustrated, there are clear trends, such as the decrease in methane fraction as the temperature increase which does not agree with the literature [65]. However, there is an observed increase in C_2-C_5 fractions with the temperature which agrees with the literature [65].The increase in lighter hydrocarbon yield can be attributed to rapid thermal cracking at higher temperatures.

The highest percentage recorded was for carbon monoxide, carbon dioxide, hydrogen sulfide and methane. Also, there is an increase in carbon monoxide and carbon dioxide fractions which is not the case in the literature where the amount of them decreases due to the increased production of light hydrocarbons at higher temperatures. The aromatic components yield (i.e. benzene) increases with temperature as other studies observed [65]. The other aromatics yield also increases with temperature but it is not consistent with other studies.

Regarding the products yield, Figure 11 shows that there is an obvious trend where the yield of liquid decreases with temperature and the maximum amount was produced at 400°C. However in other studies, liquid yield increases to a certain level and reaches its maximum around 450°C; then it decreases as the temperature increases. For gases, the trend is consistent with the literature as the yield increases with temperature due to rapid cracking of tire rubber at higher temperatures. However, the percentage of gases is significantly different from the literature which explained by the failure of simulation model to represent pyrolysis reaction.

The char consists mainly of carbon black, solid hydrocarbons and tire additives, and for this, it is not expected to have a significant loss or change in char yield with temperature except for volatilization of solid hydrocarbons at higher temperatures and that is achieved in this model.
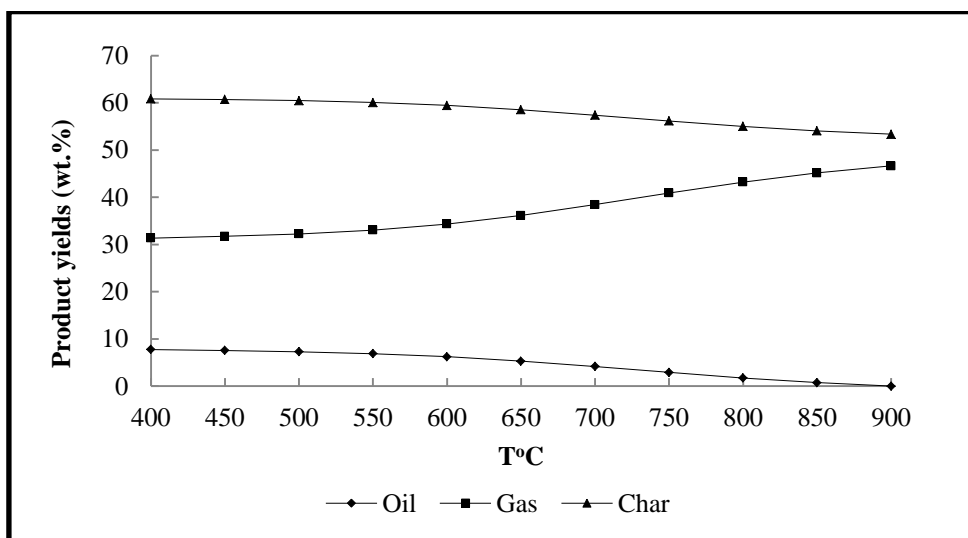
Figure 11 Effect of temperature on product yields

Chapter 3: Pyrolysis Process Exergy Analysis

As stated earlier, exergy evaluates the quality of energy by calculating the obtainable work when a process or system reaches a thermodynamic equilibrium with the surroundings which is an interpretation of second law of thermodynamics. Exergy analysis is used to identify which components work with significant inefficiencies and then gives options to improve process performance.

In this work, the kinetic and potential exergy of the streams are neglected and the exergy of working fluids is determined completely by the physical and chemical exergy. The physical exergy is defined as the work obtained from matching a stream to the pressure and the temperature of the environment. However, the chemical exergy identifies the work obtained from bringing a component or a mixture to equilibrium with its surroundings. An exergetic analysis of a pyrolysis process was conducted at a component level by defining the exergy of each stream and then calculating exergetic efficiency ψ.

The exergy analysis presented in this work is commonly used in different industrial chemical processes [67] . Relevant processes such as cement production were used to relate analysis of the pyrolysis process [68] [69] [70].The exergy balance was conducted around the pyrolysis reactor where the chemical and physical exergy were calculated for inlet streams (waste tires, heating fuel) and for outlet streams (gases and char) as illustrated in Figure 12.
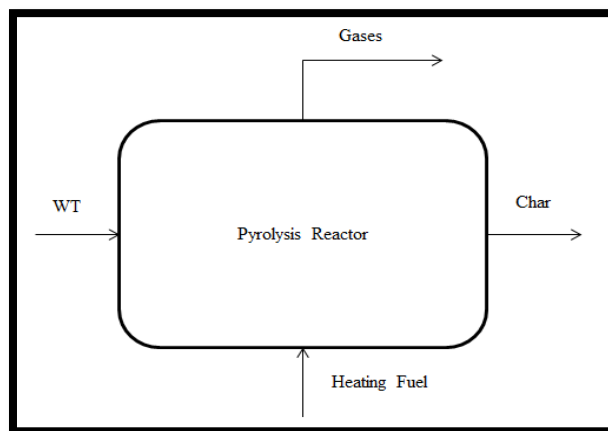
Figure 12 Inlets and outlets of pyrolysis process

3.1 Mass and Energy Balance

Mass and energy balances were conducted around the pyrolysis rotary kiln reactor and expressed on a basis of 1 kg of waste tires. The calculations were based on the following assumptions:

- The reactor works at steady state conditions (atmospheric pressure and 450°C).
- The compositions of the products (Table B.1 in Appendix B) and physical properties (Table B.2, 3) are constant.
- All gasous streams are assumed to be ideal gases.
- The fuel used for heating is assumed to be heavy fuel oil with properties and ultimate analysis represented in Appendix B (Table B.4).
- The ultimate analysis of char is assumed from the literature and presented in Appendix B (Table B.4).
- The environment temperature is assumed to be 298.15 K and the outlet temperature of the products is assumed to be 723.15 K.

The energy balance equation of the pyrolysis process is conducted around the reactor as:

$$Q_{Py} = H_{char}^o + C_{P_{char}}(T - T_o) + \sum [H_{pr}^o + \int_{T_o}^{T} C_P(T)dT] - (C_{P_{tire}} * T_{in}) \quad Eq.(2.1)$$

where Q_{py} is the pyrolysis heat, and $H^o{}_{char}$ and $H^o{}_{Pr}$ are the standard heat of formation of char and gaseous products. T_o is the reference temperature (298.15 K) and Cp_{tire} and Cp are the heat capacity of the tires and the char respectively. The physical properties used for energy balance calculation are presented in Appendix B. Table 10 shows the results of the mass and energy balance based on 1 kg of WT.

Table 10 Mass and energy balance results

Stream	Mass Balance (kg) [3]	Energy Balance (kJ/kg$_{tire}$)
Tires	1	3.85E+02
Gases	0.587	-1.51E+06
Char	0.413	-5.5E+06
Fuel	219.36	-

3.2 Chemical Exergy of the Streams

There are different equations to calculate the chemical exergy of the components depending on their physical state. For gases equation (1.12) is used, while equation (1.13) is used for solids. The standard chemical exergy of the components in each stream is presented in Appendix B (Table B.5). For some components, the chemical exergy was calculated using equation (1.14) utilizing the Gibbs free energy and combustion reaction for each component. The data used is presented in Appendix B (Table B.6). The chemical exergy of each stream of the pyrolysis process is presented in Table 11.

Table 11 Chemical exergies of pyrolysis process streams

Stream	Component	Chemical Exergy (kJ/kg)
Waste Tires	Tires	3.9E+04
Gases	1-Butene	8.56E+02
	1,3 Butadine	1.11E+01
	n-pentane	5.78E+02
	1-pentene	4.72E+00
	Benzene	2.12E+02
	Naphthalene	9.16E+02
	Fluorene	-2.30E-02
	H_2S	4.96E+01
	N_2	2.47E+00
	CO_2	5.84E+02
	Methylpropylene	2.84E+02
	CO	4.65E+03
	n-decane	8.24E-02
	Trans-2-pentene	9.81E-01
	Cis-2-butene	3.57E+00
	2-Methyl-2-butene	1.69E+00
	2-Methyl-1-butene	2.75E-01
	Isoprene	7.47E+00
	n-Nonacosane	1.25E-01
	n-Triacontane	1.79E-02
	n-Dotraiacontane	4.41E-02
	Phenanthrene	7.68E+01

Table 11 (Continued)

Stream	Component	Chemical Exergy (kJ/kg)
Gases	Anthracene	2.88E+02
	Fluoranthene	1.84E+02
	Pyrene	1.13E+01
	Chrysene	2.25E+02
	H_2O	1.65E+01
	Ethane	3.35E+03
	Ethene	2.18E+03
	Propane	2.80E+03
	Propene	3.73E+03
	n-butane	6.79E+02
	trans-2-butene	3.41E+00
	Methane	4.85E+03
	n-undecane	1.18E-01
	n-dodecane	1.14E-01
	n-tridecane	1.25E-01
	n-tetradecane	1.42E-01
	n-pentadecane	3.52E-01
	n-hexadecane	1.63E-01
	n-heptadecane	3.85E-01
	n-octadecane	6.01E-04
	n-nonadecane	6.72E-02
	n-eicosane	6.00E-02
	n-heneicosane	5.38E-02
	n-docosane	5.01E-02
	n-tetracosane	1.06E-01
	n-pentacosane	1.18E-01
	n-hexacosane	9.99E-02
Total		2.11E+04
Char	Char	3.3E+04
Fuel	Heavy oil	4.3E+07

3.3 Physical Exergy of the Streams

For gases, equation (1.10) was used to calculate the physical exergy and for solids equation (1.11) was used. The physical exergy of the pyrolysis process streams are presented in Table 12.

Table 12 Physical exergies of pyrolysis process streams

Stream	Component	Physical Exergy (kJ/kg)
Waste Tires	Tires	4.49E-01
Gases	1-Butene	2.1E+04
	1,3 Butadine	1.9E+04
	n-pentane	3.2E+04
	1-pentene	3.4E+03
	Benzene	2.4E+04
	Naphthalene	3.1E+04
	Fluorene	5.4E+03
	H_2S	7.7E+02
	N_2	4.8E+03
	CO_2	1.9E+02
	Methylpropylene	2.3E+04
	CO	1.8E+02
	n-decane	5.9E+04
	Trans-2-pentene	4.7E+02
	Cis-2-butene	4.7E+02
	2-Methyl-2-butene	3.8E+02
	2-Methyl-1-butene	4.8E+02
	Isoprene	4.97E+02
	n-Nonacosane	5.4E+02
	n-Triacontane	5.9E+02
	n-Dotraiacontane	5.7E+02
	Phenanthrene	3.4E+02
	Anthracene	3.5E+02
	Fluoranthene	3.5E+02
	Pyrene	3.4E+02
	Chrysene	3.5E+02
	H_2O	3.4E+02
	Ethane	5.4E+02

Table 12 (Continued)

Stream	Component	Physical Exergy (kJ/kg)
Gases	Ethene	4.5E+02
	Propane	5.2E+02
	Propene	4.6E+02
	n-butane	5.2E+02
	trans-2-butene	4.7E+02
	Methane	1.2E+03
	n-undecane	5.1E+02
	n-dodecane	5.1E+02
	n-tridecane	5.1E+02
	n-tetradecane	5.1E+02
	n-pentadecane	5.1E+02
	n-hexadecane	5.1E+02
	n-heptadecane	5.1E+02
	n-octadecane	5.1E+02
	n-nonadecane	5.1E+02
	n-eicosane	5.1E+02
	n-heneicosane	5.3E+02
	n-docosane	5.4E+02
	n-tetracosane	5.4E+02
	n-pentacosane	5.4E+02
	n-hexacosane	5.4E+02
Total		2.4E+05
Char	Char	6.5E-01
Fuel	Heavy oil	6.3E-01

To evaluate the pyrolysis process internal exergy losses, irreversibility was calculated using equation (1.7). The inlet and outlet streams total exergy was evaluated using equation (1.8) based in 1 kg of waste tires. Also, general and useful exergy efficiencies were evaluated using equation (1.15-1.16). The results are presented in Table 13.

Table 13 Inlet and outlet total exergy and process irreversibility

Stream	Exergy (kJ)
Waste tires	39326.04
Fuel	9.4E+09
Gases	1.38E+04
Char	1.37E+04
Irreversibility (kJ)	
1.18E+04	
Exergy Efficiency	
69.9 %	
Useful Exergy Efficiency	
35.2%	

As illustrated in Table 13, the exergy balance of the rotary kiln shows that 30.1% of the inlet exergy is destroyed in the process due to irreversibility. The pyrolysis process exergetic efficiency is 69.9%, which is considered within the range for gasification processes [71] [72] [73] [74]. The useful exergetic efficiency was found to be 35.2% which means that only the exergy of the gases' stream can be utilized as it is considered the desirable product from the process.

3.4 Improvement Potentials

The pyrolysis reactor is responsible for a significant percentage of the total exergy destruction due to chemical reactions. However, because of limitation on temperature range if the oil is the targeted where the maximum oil yield is around 500 $^{\circ}$C it will be difficult to improve the efficiency. Using a different reactor type also will not change the exergy destruction although it will change the oil yield and product composition. The only improvement potential is by reducing the electricity consumption of the pyrolysis plant. Using non-condensable gases as fuel for the pyrolysis process did not improve the exergetic efficiency. In fact, the exergetic efficiency decreased by 9.08% due to indirect heating in the rotary kiln reactor in which heating fuel does not contribute to the exergy balance.

Chapter 4: Pyrolysis Life Cycle Assessment

The plant capacity of pyrolysis is assumed to be 10 tons per day of waste tires and 45.1% of oil is assumed to be produced from waste tires. Fuel production from WT includes WT transportation, WT shredding, WT pyrolysis, oil recovery, char collection and product distribution and use. In the step of WT shredding, steel is removed from the tires; then the tires are chopped into small pieces. In the pyrolysis step, WTs produce approximately 13.6% of non-condensable gases, 45.1% of oil and 41.3% of char in a rotary kiln reactor at $450^{o}C$ and ambient pressure. Then, the produced vapors are recovered by a condenser. The char and ash is removed from the reactor.

4.1 Pyrolysis LCA Goal and Scope Definition

The goal of this study is to identify and assesses the environmental impacts and consequences of all the stages in the process of production of liquid fuel from waste tires by pyrolysis. ISO 14040 and ISO 14044 standards and methods were used as they are the most appropriate for this analysis. The analysis was conducted in the LCA software SimaPro 7.3.2. Also, a sensitivity analysis was carried out to evaluate the effect of the change in energy used in the production process. The results are useful for the environmental agencies in UAE and waste management and research centers.

4.1.1 Functional unit. The functional unit in this study is 1 kg of WT converted to fuel in the pyrolysis plant. Energy consumption, materials and all emissions are related to the functional unit.

4.1.2 Cut off. The following are the limitations of the study:

- All tires were obtained from a solid waste dumping area; the transportation from the shops to the dumping area was not considered.
- Construction of the plant and land use was not considered.
- Tire production and capital goods manufacturing were eliminated due to lack of information.
- Materials storage impacts were considered to be negligible due to immediate processing.

4.1.3 System boundaries. The life of a pyrolysis plant is assumed to be 10 years [75]. Also, the life of produced fuel is assumed to be the same. The production and the use of the pyrolytic oil are carried out in the UAE but the capital goods are brought from abroad. The system boundary is illustrated in Figure 13.
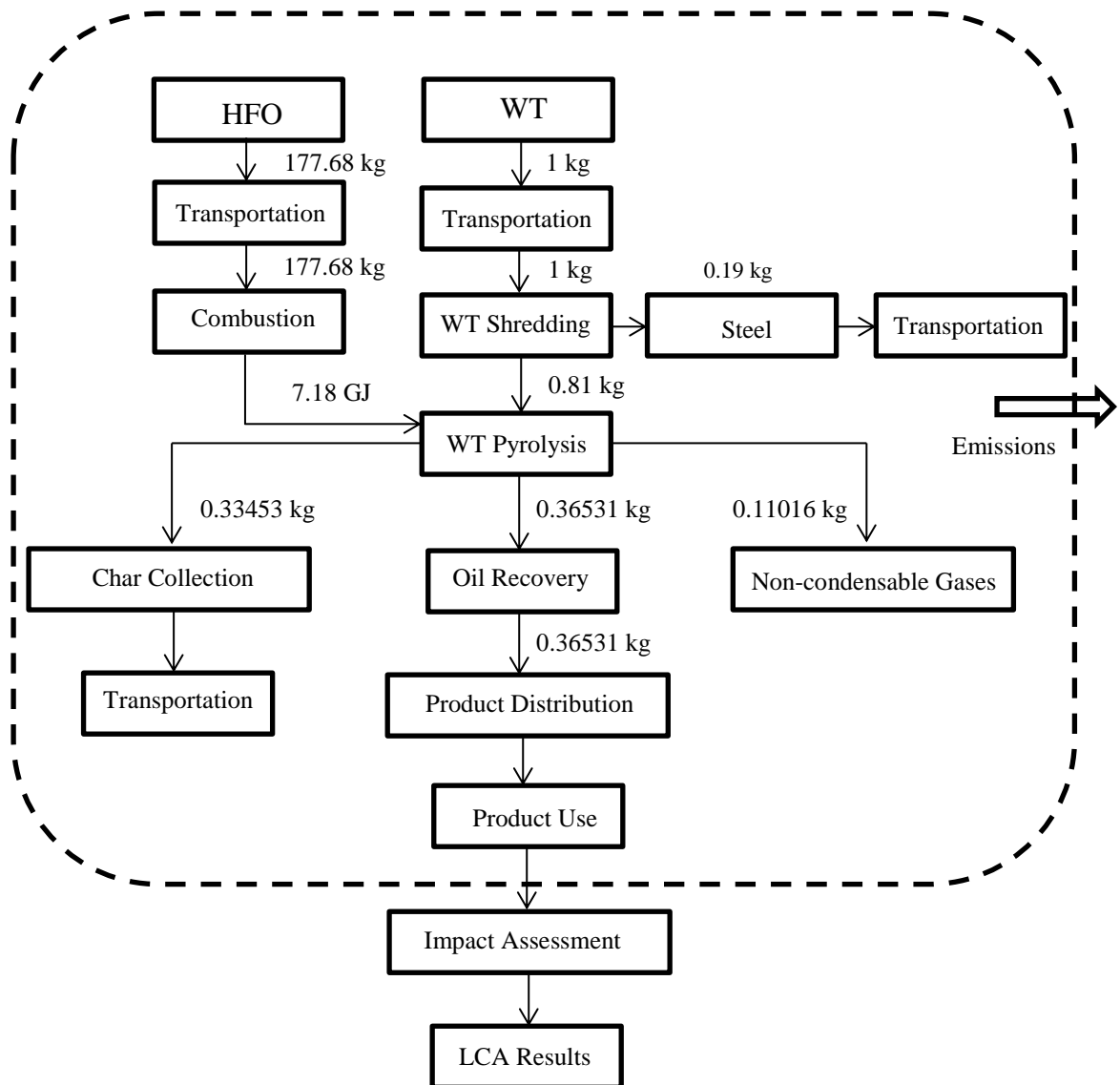
Figure 13 System boundary of WT pyrolysis

4.2 Impact Assessment

In this study, the characterization methodology used is the environmental design of industrial products (EDIP-2003). This method represents 19 impact categories. Some of the impact category indicators are: global warming potential (GWP), acidification potential (AP), eutrophication potential (EP), ozone depletion

potential (ODP), smog formation potential (SFP), human toxicity potential (HTP), and terrestrial eutrophication potential (TECP). The environmental impacts were investigated using SimaPro 7.3.2 LCA software [76].

4.3 Inventory Analysis

In the inventory analysis stage, the data collection and calculations were conducted. Reasonable assumptions were made and some references were used in this step. The calculations carried out for the inventory data are illustrated in Appendix C. The inventory data for the processes are presented in Table 14.

4.3.1 Heating fuel transportation. For this analysis, heavy oil is assumed to be the heating fuel for the pyrolysis process. It is assumed that the heavy oil is transported by a diesel powered 27 ton of capacity truck to a distance of 6.5 km. Input to this step is the heavy oil and diesel for the truck and the outputs are the delivered fuel and emissions from transportation. The emissions generated from the transportation are calculated in SimaPro.

4.3.2 WT transportation. Waste tires were assumed to be transported by a diesel powered 27 ton loading capacity single unit truck for a distance of 32 km. The inputs in this process are WTs from a solid waste dumping area and truck diesel. The outputs are the WTs delivered to the plant and emissions to air from transportation which will be calculated in the software.

4.3.3 HFO combustion. Heavy oil is the heating fuel for the pyrolysis process. The input of the combustion step is the delivered HFO and the output is the heat needed for the pyrolysis reaction and combustion emissions to the air.

4.3.4 WT shredding. In this unit, the steel wire in the WTs is removed using a steel wire separator; then the tires are shredded into small pieces using a ring cutter, strip cutter, and rim cutter. The process requires a total energy of 0.10735 MJ for electricity.

4.3.5 Pyrolytic oil production. The inventory analysis of this step consists of WT pyrolysis, oil recovery, and char and non-condensable gas collection. The inputs are shredded WT and the fuel for heating and the outputs are pyrolytic oil, char, and non-condensable gases which are considered here as emissions to air. Electricity is

used for WT feeding and char removal. WT pyrolysis produces 13.6% non-condensable gases, 45.1% pyrolytic oil and 41.3% char.

4.3.6 Pyrolytic oil distribution. In this step, the pyrolytic oil was assumed to be transported from the pyrolysis plant to the cement plant by a diesel powered 27 ton capacity truck which will be used as a heating fuel. The total distance was calculated to be 6.6 km on a road trip. Inputs to the process were pyrolytic oil and the diesel for the truck. The outputs were the delivered pyrolytic oil and emissions to the air.

4.3.7 Char distribution. It is assumed that the char is transported from the pyrolysis plant to a carbon factory in a diesel powered 27 ton capacity truck. The total distance is around 30.9 km. All calculations are illustrated in Appendix C. The inputs for this step are the char and diesel for the truck and the outputs are the delivered char and the emissions from transportation.

4.3.8 Steel distribution. In this step, the steel extracted from the WTs is transported from the pyrolysis plant to a steel manufacturing company in a diesel powered 27 ton capacity truck for a total distance of 69.7 km. The inputs are the steel and the diesel for the truck where the outputs are the delivered steel and the emissions to the air.

4.3.9 Pyrolytic oil consumption. Pyrolytic oil is used as heating fuel in the cement industry. The approximate GCV of the oil is around 42.66 MJ kg^{-1} [29]. The data of emissions from the combustion of pyrolytic oil is presented in Table 14.

Table 14 Inventory data of WT pyrolysis process (based on 1 kg of WT)

Process	Input	Amount	Output	Amount
Heavy Fuel Oil Transportation	Heavy Fuel Oil	177.68 kg	Delivered HFO	177.68 kg
	Tonnskilometers	0.0132 tkm		
WT Transportation	WT	1 kg	Delivered WT	1 kg
	Tonnskilometers	0.0319 tkm		
WT Shredding	Delivered WT	1 kg	Shredded WT	0.81 kg
	Electricity for Steel Wire Separator	0.036 MJ	Steel	0.19 kg

Table 14 (Continued)

Process	Input	Amount	Output	Amount
WT Shredding	Electricity for Ring Cutter	0.0216 MJ	PM <10 μm	4.93E-7kg
	Electricity for Strips Cutter	0.016 MJ	PM<2.5 μm	3.28E-7kg
	Electricity for rim cutter	0.03375 MJ		
HFO Combustion	Delivered HFO	177.68 kg	Combustion Heat	7.18 GJ
			NOx	1.28 kg
			CO	0.033 kg
			Soot	0.4264 kg
			Particulates	0.617 kg
Pyrolytic Oil Production	Electricity	0.1642 MJ	Pyrolytic Oil	0.36351 kg
	Shredded WT	0.81 kg	Char	0.33453 kg
	Heavy Oil	177.68 kg	Non-condensable gases	0.1106 kg
			CO_2	7.16E-3 kg
			H_2S	2.313E-4 kg
			CO	0.0522 kg
			Ethane	7.38E-3 kg
			Ethene	4.957E-3 kg
			Propane	6.28E-3 kg
			Propene	8.59E-3 kg
			n-butane	1.54E-3 kg
			trans-2-butene	3.3E-4 kg
			Methane	9.91E-4 kg
			1-Butene	1.983E-3 kg
			1,3 Butadine	4.41E-4 kg
			Methylpropylene	6.61E-4 kg
			Trans-2-pentene	1.1E-4 kg
			Cis-2-butene	3.3E-4 kg
			2-Methyl-2-butene	2.2E-4 kg

Table 14 (Continued)

Process	Input	Amount	Output	Amount
Pyrolytic Oil Production			2-Methyl-1-butene	3.3E-5 kg
			n-pentane	1.32E-3 kg
			1-pentene	1.102E-5 kg
			Benzene	5.508E-4 kg
Pyrolytic Oil Distribution	Pyrolytic Oil	0.36531 kg	Delivered PO	0.36531 kg
	Tonnskilometers	0.00241 tkm		
Char Distribution	Char	0.33453 kg	Delivered Char	0.33453 kg
	Tonnskilometers	0.0103 tkm		
Steel Distribution	Steel	0.19 kg	Delivered Steel	0.19 kg
	Tonnskilometers	0.0132 tkm		
Pyrolytic Oil Consumption	Delivered PO	0.36531 kg	Heat	15.584 MJ
			NOx	1.3714E-3 kg
			CO	7.169E-5 kg
			Soot	8.767E-4 kg
			Particulates	1.34E-3 kg

4.4 Results and Discussion

Figure 14 shows the impacts of pyrolytic oil production and application. Each impact category represented as a percentage. As illustrated in Figure 14, the major environmental effects of the process are the emissions from the combustion process of heavy fuel oil and pyrolytic oil. The effect of transportation and electricity needed are negligible with respect to other processes. The highest contributions to GWP and ozone depletion are the emissions of heavy oil combustion and chemicals in the heavy oil with 34.4% for each. On the other hand, emissions from pyrolytic oil and its composition contribute with 15.5% for each. Moreover, heavy fuel oil combustion to produce the heat needed in the pyrolysis reactor is the main contributor in most impact categories (i.e. 63 % of terrestrial eutrophication and aquatic eutrophication). The rest of the impact categories recorded almost the same contribution for each process.
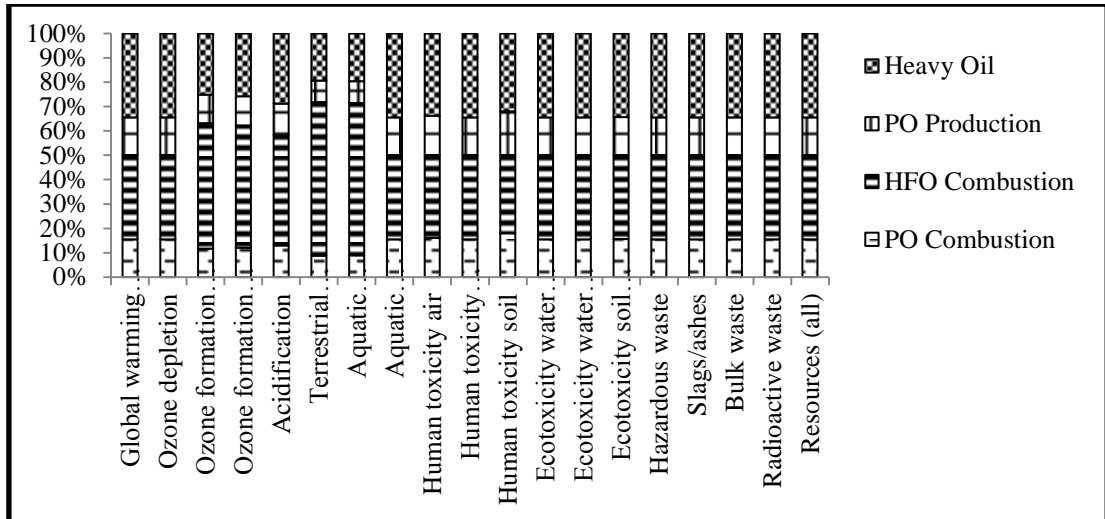
Figure 14 Characterization of impacts of pyrolytic oil production and application

In order to evaluate the significance of each impact category in the characterization step, the impact indicators were divided by a reference number. This procedure is the normalization step was defined earlier. In the method used (EDIP 2003), the reference number used for an impact category is one average European person per year. As Figure 15 shows, radioactive waste has a normalized score of 0.73 and ozone depletion comes second with a score of 0.25. The other categories have normalized scores less than 0.1. Although pyrolysis process emissions seem to make a big contribution to GWP, the results show that the normalized score is small, around 0.03.
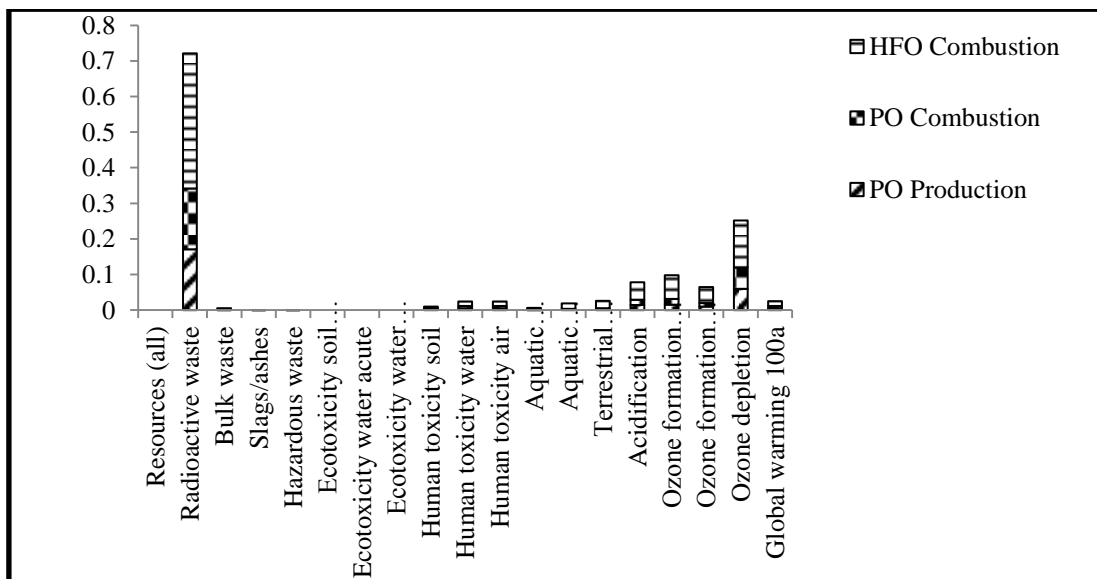
Figure 15 Normalization of impacts of pyrolytic oil production and application

In Figure 16, a summary of the single score in mili-points of the most significant impact categories for pyrolytic oil production and application are presented. The most dominant process is HFO combustion where the emissions to air are contributing to ozone depletion and human toxicity impact categories. HFO has the second highest contribution in all impact categories which suggests that it is better to study the possibility of using another fuel to produce the energy needed for the pyrolysis reactor.
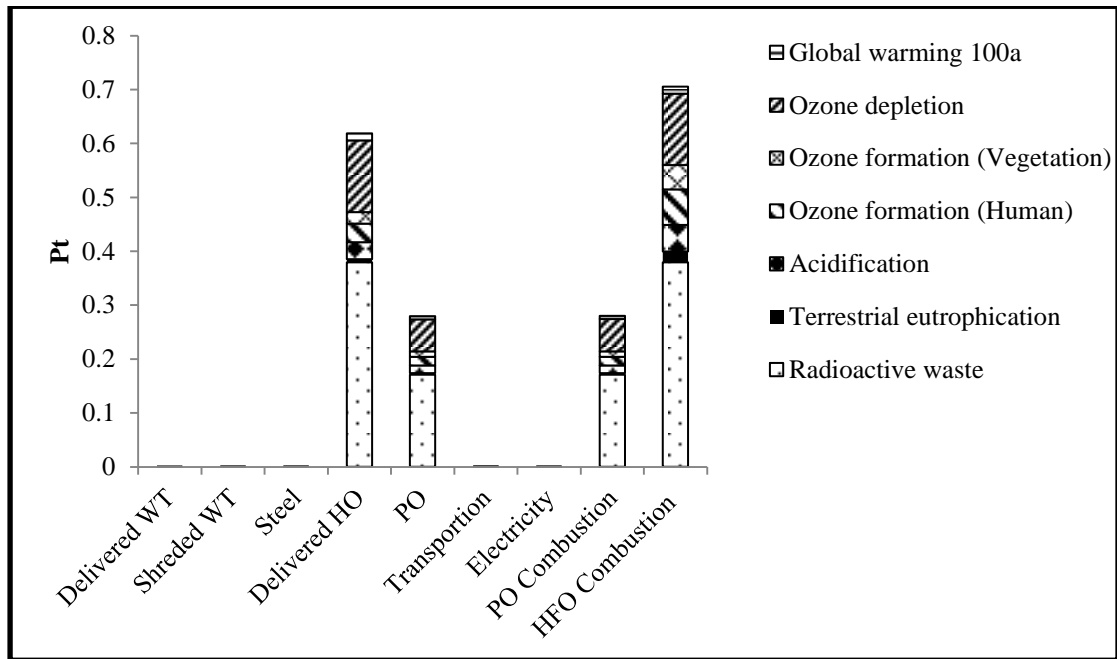
Figure 16 Single scores of impact categories

To understand the effect of HFO on the impact categories, a sensitivity analysis is required to evaluate how changing some parameters in the LCA will affect the impact categories.

The first parameter changed is the heating fuel used in the pyrolysis reactor, where the non-condensable gases will be recycled instead of using HFO. As a result, transportation of the HFO will be eliminated, and the combustion of HFO, the fuel will be replaced by the non-condensable gases which have an average CV of 42.5 MJ/m^3 [3]. Moreover, the emissions will be recalculated with respect to non-condensable gases. Also, the emissions in pyrolytic oil production were eliminated as it was assumed that all non-condensable gases will be released to environment. All related calculations are illustrated in Appendix C. The modified inventory data are presented in Table 15.

Table 15 Inventory data of WT pyrolysis process with NCG as heating fuel (based on 1 kg of WT)

Process	Input	Amount	Output	Amount
WT Transportation	WT	1 kg	Delivered WT	1 kg
	Tonnskilometers	0.0319 tkm		
WT Shredding	Delivered WT	1 kg	Shredded WT	0.81 kg
	Electricity for Steel Wire Separator	0.036 MJ	Steel	0.19 kg
	Electricity for Ring Cutter	0.0216 MJ	PM <10 μm	4.93E-7kg
	Electricity for Strips Cutter	0.016 MJ	PM<2.5 μm	3.28E-7kg
	Electricity for rim cutter	0.03375 MJ		
NCG Combustion	NCG	228.3 kg	Combustion Heat	7.58 GJ
			NOx	0.667 kg
			CO	0.0349 kg
			Soot	0.548 kg
			Particulates	0.652 kg
Pyrolytic Oil Production	Electricity	0.1642 MJ	Pyrolytic Oil	0.36351 kg
	Shredded WT	0.81 kg	Char	0.33453 kg
	Heavy Oil	177.68 kg	NCG	0.11016 kg
Pyrolytic Oil Distribution	Pyrolytic Oil	0.36531 kg	Delivered PO	0.36531 kg
	Tonnskilometers	0.00241 tkm		
Char Distribution	Char	0.33453 kg	Delivered Char	0.33453 kg
	Tonnskilometers	0.0103 tkm		
Steel Distribution	Steel	0.19 kg	Delivered Steel	0.19 kg
	Tonnskilometers	0.0132 tkm		

Table 15 (Continued)

Process	Input	Amount	Output	Amount
Pyrolytic Oil Consumption	Delivered PO	0.36531 kg	Heat	15.584 MJ
			NOx	1.3714E-3 kg
			CO	7.169E-5 kg
			Soot	8.767E-4 kg
			Particulates	1.34E-3 kg

As illustrated in Figure 17, there is a significant positive change on the impact categories when the non-condensable gases were used as a heating fuel in the pyrolysis reactor instead of heavy fuel oil. First of all, there is no effect on the hazardous waste, bulk waste and radioactive waste impact categories; this can be attributed to the fact that there is a significant reduction in the emissions to air and the type of components that have been emitted to the air. The highest contribution is recorded to ozone depletion, ozone formation, eutrophication and acidification is from NCG combustion which is due to the high amount of NOx and CO emitted to the air. The second significant contribution to the impact categories comes from the electricity or power needed to operate the equipment in the plant. Its affects is mainly on human toxicity and eco-toxicity of water and soil. Then, the effect of transportation is considered significant where the emissions from diesel combustion to air are contributing to the ozone depletion, eutrophication and ash impact categories.
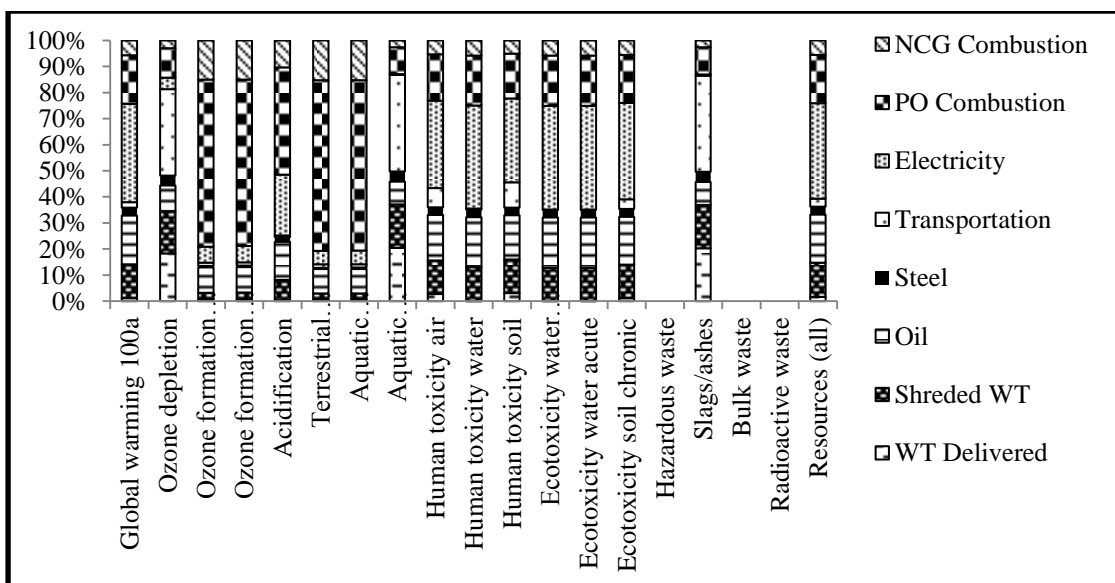
Figure 17 Characterization of impact categories of PO production and application with NCG as heating fuel

Figure 18 shows the normalization of the impacts based on the EDIP 2003 method. As presented, the environmental impacts were only concentrated in five categories: ozone formation (vegetation and human), acidification, terrestrial eutrophication and aquatic eutrophication.
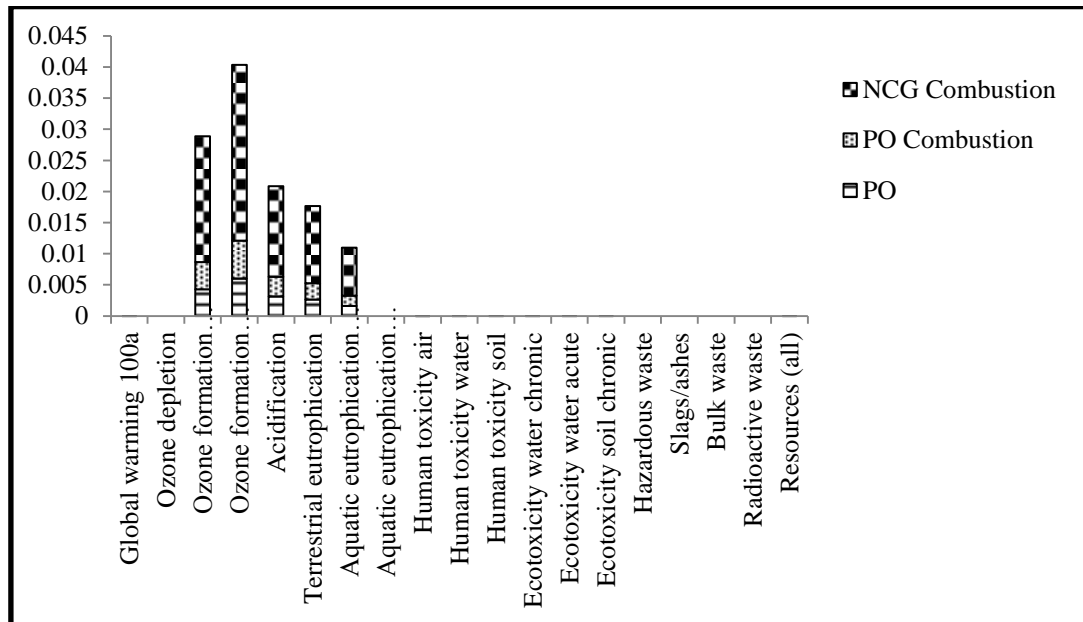
Figure18 Normalization of impact categories of PO production and application with NCG as heating fuel

The highest normalization score was 0.04 which is recorded for ozone formation impact on humans, followed by the contribution of the pyrolysis process on ozone formation (vegetation), then acidification, terrestrial eutrophication, and aquatic eutrophication, respectively. The highest contributing process is NCG combustion as stated earlier due to the high amount of CO and NOx. Compared to the normalization of impact of pyrolysis process with HFO as a heating fuel, there is a significant difference where the highest score in Figure 15 was recorded for radioactive waste impact. However, replacing the heating fuel and recycling the NCG improved the overall performance of the process with respect to the environmental impacts.

Moreover, a single score representation of the result was conducted to give a more detailed picture on the consequences of changing the heating fuel. Figure 19 shows that the most damaging product is the emissions to air produced from the combustion of the non-condensable gases. Compared to the basic process, there is a significant difference in the range of the eco-points (Pt) where in the basis process the highest score was 0.75 mPt. Pt is defined as a measuring unit equal to one thousandth of the annual environmental impact attributed to one a European individual [77].

However, in the modified process (NCG as heating fuel) the highest score recorded is 100 mPt. This can be attributed to the higher amount produced in the modified process of CO, NOx, and soot.

To have a clear picture of the differences which occurred when the heavy fuel oil was replaced by the non-condensable gases, a comparative life cycle assessment between the base process (heating with HFO) and the second scenario (heating with NCG) was conducted.
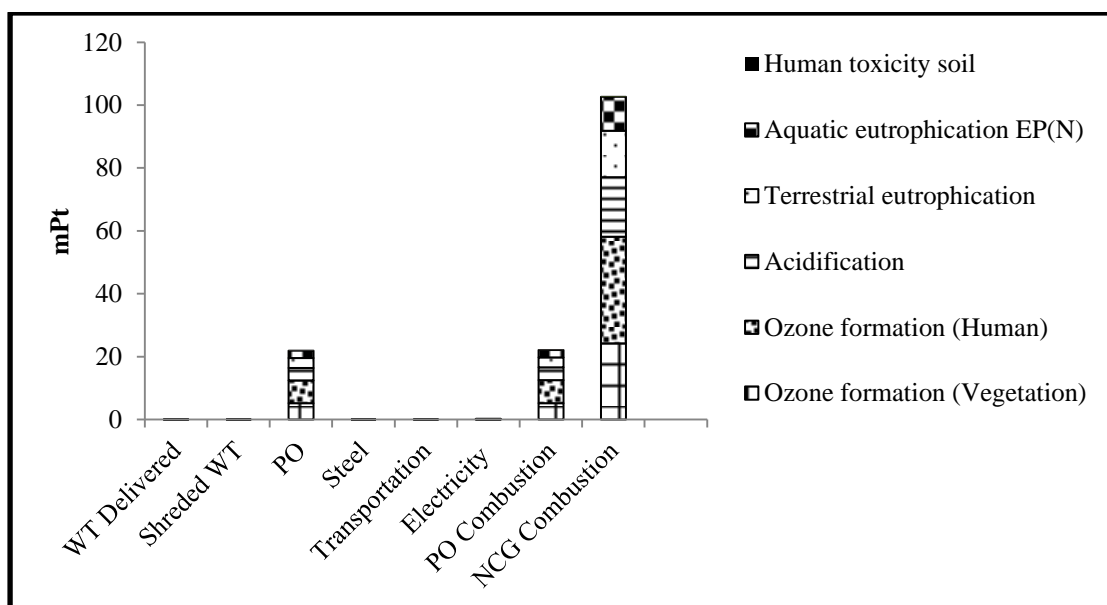
Figure 19 Single scores of impact categories of pyrolysis process with NCG as heating fuel

Figure 20 shows a significant reduction in the impact categories of the pyrolysis process with NCG. As illustrated earlier, this is due to the reduction in the emissions of hazardous materials to air, soil and water. A normalization reference was also used to give a better perception of the significant improvement obtained from using NCG as the heating fuel. Figure 21 shows the normalization of the impacts in the two scenarios where it is clear that using the normalization score provided the importance of each impact. The radioactive waste impact scored the highest for both scenarios; however, it is significantly higher in the base process than the second scenarios. This can be attributed to the fact that in the base scenario emitting the NCG from the pyrolysis reactor to the air had a massive negative effect on the environment.
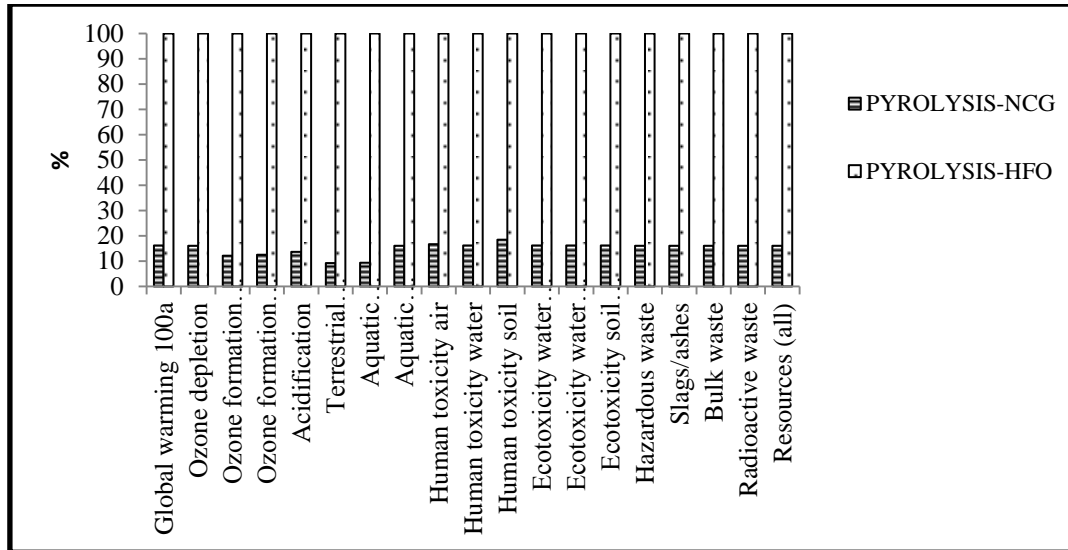
Figure 20 Characterization of impacts of the comparison between the Basis process and the second scenario
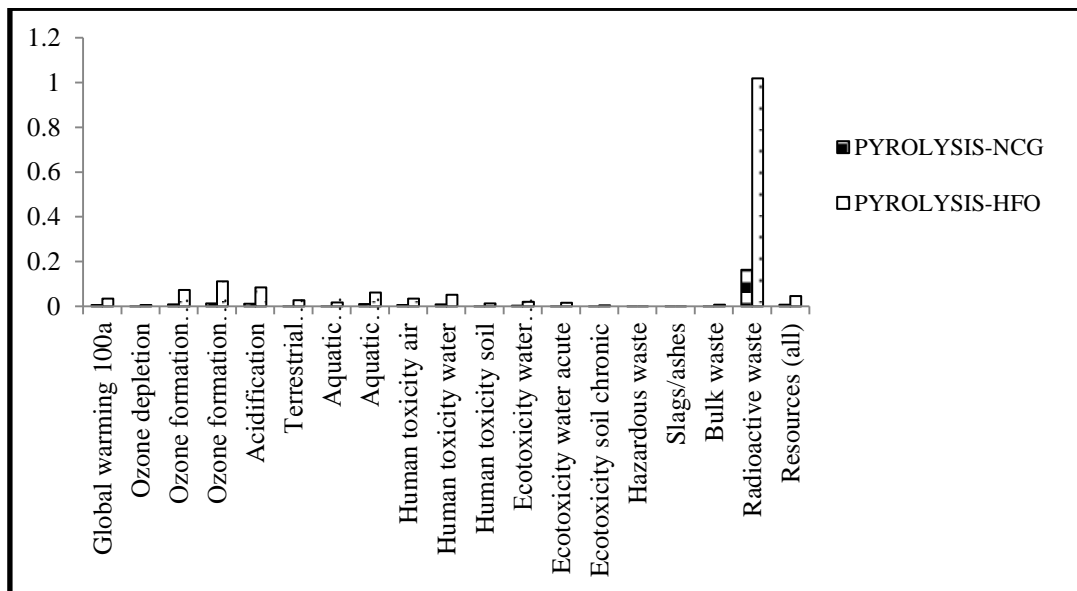
Figure 21 Normalization of impacts of the comparison between the basis process and the second scenario

Figure 22 represents the single score of the impacts in Pt. As illustrated, there is a substantial reduction in the impacts of the second scenario. Although, in the second scenario there is a significant reduction in the use of fossil fuels, the radioactive waste impact still has a recognizable contribution in the total environmental impact. The same observation is obtained for the aquatic eutrophication impact where the contribution to the total environmental impact considered the same as the base process but with a smaller score. This is due to the significant amount of nitric oxides that has been produced from the combustion process.

It is safe to say that recycling NCG to provide the energy needed in the pyrolysis reaction is the preferable choice due to its improvement on the environmental impact.
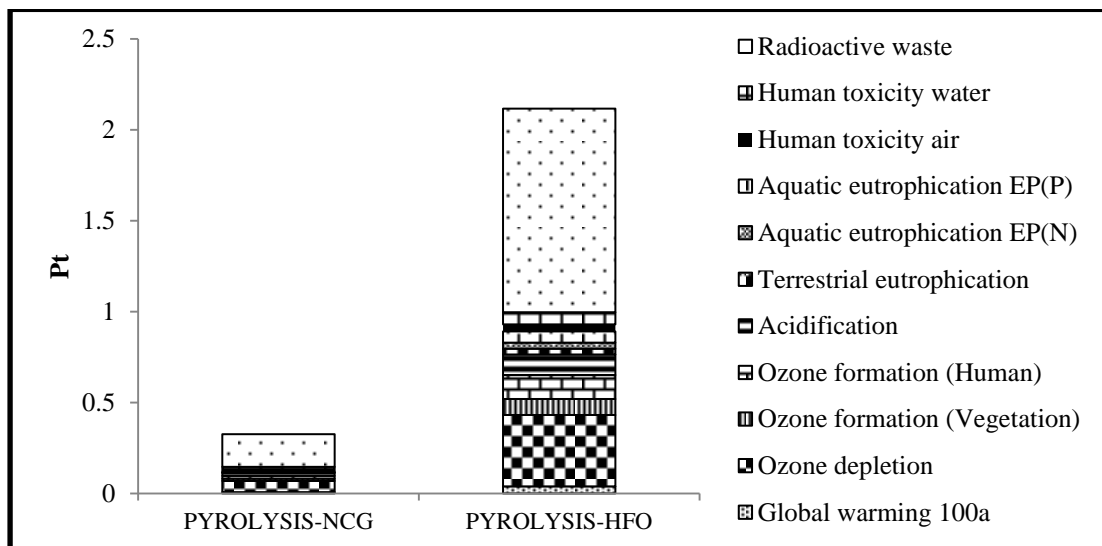
Figure 22 Single Scores of Impacts of the Comparison between the Basis Process and the Second Scenario

Chapter 5: Conclusions and Recommendations

5.1 Conclusions

In this study, the waste tires pyrolysis process in a rotary kiln reactor was conducted. A steady state equilibrium model in computer aided software (ASPEN Plus$^®$ 8.4) was developed where the pyrolysis process was simulated at 450°C and atmospheric pressure. Then, the model was validated by experimental data from the literature and a sensitivity analysis was conducted to study the effect of temperature on the yield of the pyrolytic oil. It was concluded that the effect of temperature on the pyrolysis product follows a certain pattern where the optimum temperature to produce highest pyrolytic oil yield was around 450-550°C. Then, as the temperature increases, the yield of pyrolytic oil decreases. However, the model results are not consistent with the literature. Therefore, the results require further study in order to improve the representation of the pyrolysis reactions in the simulation and create a model that succeeds in predicting the performance of the pyrolysis reactor.

Moreover, energy and mass balance and an exergy analysis were performed around the pyrolysis reactor. The waste tire pyrolysis process achieved an exergetic efficiency of 69.9% which is considered within the range for pyrolysis processes. Also, 30.1% of the inlet exergy was destroyed due to irreversibility and 35.1% of the useful exergetic efficiency was recorded. The pyrolysis reactor is responsible for a significant percentage of the total exergy destruction due to the chemical reactions. Improvements can be achieved by reducing the consumption of energy and electricity needed in the process.

Finally, a life cycle assessment of the production of pyrolytic oil via a pyrolysis plant and its use was conducted in SimaPro 7.3.2 to investigate the contribution of the process on the total environmental impacts. The results showed that the process has a significant contribution in GWP, ozone depletion and formation, and human toxicity via air. The dominant contribution is from HFO combustion. Thus, a sensitivity analysis was performed to study the effect of replacing the heating fuel. According to the sensitivity analysis results, there is a significant reduction on the environmental impact when the non-condensable gases recycled to the process for heating purposes.

5.2 Recommendations

First of all, more experimental work needs to be conducted to evaluate the composition of pyrolytic oil and the effect of reaction parameters on the composition and yield. Then, a predictive model related to experimental results, especially for waste tire pyrolysis needs to be created to identify the product components and their relative content. In addition, an extensive exergy analysis for the pyrolysis process on an indirect heated rotary kiln needs to be conducted to investigate the contribution of each part in the plant in exergy destruction to find ways for improvement. Finally, more data needs to be collected regarding the process to conduct a comprehensive life cycle assessment to be able to understand more about the impact of this process on the environment.

References

[1] O. Dogan, M. Bahattin Celik and B. Ozdalyan, "The Effect of Tire Derived Fuel/Diesel Fuel Blends Utilization on Diesel Engine Performance and Emissions," *Fuel,* vol. 95, pp. 340-346, 2012.

[2] S. Murugan, M. Ramaswamy and G. Nagaranian, "The Use of Tyre Pyrolysis Oil in Diesel Engines," *Waste Management,* vol. 28, no. 12, pp. 2743-2749, 2008.

[3] P. T. Williams, "Pyrolysis of Waste Tyres: A Review," *Waste Management,* vol. 33, no. 8, pp. 1714-1728, 2013.

[4] D. Leung and C. Wang, "Fluidized-Bed Gasification of Waste Tire Powders," *Fuel Processing Technology,* vol. 84, no. 1-3, pp. 175-196, 2003.

[5] H. Karatas, H. Olgun, B. Engin and F. Akgun, "Experimental Results of Gasification of Waste Tire with Air in a Bubbling Fluidized Bed Gasifier," *Fuel,* vol. 105, p. 566–571, 2013.

[6] S. Portofino, A. Donatelli, P. Iovane, C. Innella, R. Civita, M. Martino, D. A. Matera, A. Russo, G. Cornacchina and S. Galvango, " Steam Gasification of Waste Tyre: Influence of Process Temperature on Yield and Product Composition," *Waste Management,* vol. 33, no. 3, pp. 672-678, 2013.

[7] A. Evans and R. Evans, "The Composition of a Tire:Typical Components," The Waste & Resources Action Programme, Banbury, 2006.

[8] M. Betancur, J. D. Martinez and R. Murillo, "Production of Activated Carbon by Waste Tire Thermochemical Degradation with CO2," *Journal of Hazardous Materials,* vol. 168, no. 2-3, p. 882–887, 2009.

[9] T. Malkow, "Novel and Innovative Pyrolysis and Gasification Technologies for Energy Efficient and Environmentally Sound MSW Disposal," *Waste Management,* vol. 24, no. 1, pp. 53-79, 2004.

[10] S. Galvango, G. Casciaro, S. Casu, M. Martino, C. Mingazzini, A. Russo and S. Portofino, "Steam Gasification of Tyre Waste, Poplar, and Refuse-Derived Fuel: A Comparative Analysis," *Waste Management,* vol. 2, p. 678–689, 2009.

[11] M. R. Islam, M. Tushar and H. Haniu, "Production of Liquid Fuels and Chemicals from Pyrolysis of Bangladeshi Bicycle/Rickshaw Tire Wastes," *Journal of Analytical and Applied Pyrolysis,* vol. 82, no. 1, pp. 96-109, 2008.

[12] S. Murugan, M. Ramaswamy and G. Nagarajan, "A Comparative Study on the Performance, Emission and Combustion Studies of a DI Diesel Engine Using Distilled Tyre Pyrolysis Oil–Diesel Blends," *Fuel,* vol. 87, no. 10-11, pp. 2111-2121, 2008.

[13] H. Aydin and C. Ikilic, "Fuel Production from Waste Vehicle Tires by Catalytic Pyrolysis and its Application in a Diesel Engine," *Fuel Processing Technology,* vol. 92, no. 5, pp. 1129-1135, 2011.

[14] D. Bunthid, P. Prasassarakich and H. Napida, "Oxidative Desulfurization of Tire Pyrolysis Naphtha in Formic Acid/H2O2/Pyrolysis Char System," *Fuel,* vol. 89, no. 9, p. 2617–2622, 2010.

[15] M. Islam, M. Islam, N. Mustafi, M. Rahim and H. Haniu, "Thermal Recycling of Solid Tire Wastes for Alternative Liquid Fuel: the First Commercial Step in Bangladesh," *Procedia Engineering,* vol. 56, pp. 573-582, 2013.

[16] H. Aydin and C. Iilkilic, "Optimization of Fuel Production from Waste Vehicle Tires by Pyrolysis and Resembling to Diesel Fuel by Various Desulfurization Methods," *Fuel,* vol. 102, p. 605–612, 2012.

[17] J. D. Martinez, N. Puy, R. Murillo, T. Garcia, M. V. Navarro and A. M. Mastral, "Waste Tyre Pyrolysis–A Review," *Renewable and Sustainable Energy Reviews,* vol. 23, pp. 179-213, 2013.

[18] N. Antoniou and A. Zabaniotou, "Features of an Efficient and Environmentally Attractive Used Tyres Pyrolysis With Energy and Material Recovery," *Renewable and Sustainable Energy Reviews,* vol. 20, pp. 539-558, 2013.

[19] O. Ortiz, N. Martinez, C. Mengual and P. Aballay, "Optimal Operation Profit of a Pilot Rotary Kiln for Charcoal Activation," *Latin American Applied Research,* vol. 37, no. 3, pp. 207-213, 2007.

[20] C. Diez, M. Sanchez, P. Haxaire, O. Martinez and A. Moran, "Pyrolysis of Tyres: A Comparison of the Results from a Fixed-Bed Laboratory Reactor and a Pilot Plant (Rotary Reactor)," *Journal of Analytical and Applied Pyrolysis,* vol. 74, no. 1-2, p. 254–258, 2005.

[21] "The Westmoreland Group," Envergent Technologies, LLC., Available: http://www.che.ncsu.edu/westmoreland/images/rapid-thermal-processing-unit-uop1.jpg. [Accessed 16 10 2013].

[22] R. E. Raj, Z. R. Kennedy and B. Pillai, "Optimization of Process Parameters in Flash Pyrolysis of Waste Tyres to Liquid and Gaseous Fuel in a Fluidized Bed Reactor," *Energy Conversion and Management,* vol. 67, p. 145–151, 2013.

[23] A. Quek and R. Balasubramanian, "Liquefaction of Waste Tires by Pyrolysis for Oil and Chemicals—A Review," *Journal of Analytical and Applied Pyrolysis,* vol. 101, p. 1–16, 2013.

[24] A. Hossain and P. Davies, "Pyrolysis Liquids and Gases as Alternative Fuels in Internal Combustion Engines –A Review," *Renewable and Sustainable Energy Reviews,* vol. 21, pp. 165-189, 2013.

[25] I. Dincer and Y. A. Cengel, "Energy, Entropy and Exergy Concepts and Their Roles in Thermal Engineering," *Entropy,* vol. 3, pp. 116-149, 2001.

[26] P. Williams, R. Bottrill and A. Cunliffe, "Combustion of Tyre Pyrolysis Oil," *Transactions of the Institution of Chemical Engineers,* vol. 76, no. 4, pp. 291-301, 1998.

[27] S. Li, Q. Yao, J. Yan and K. Cen, "Pilot-Scale Pyrolysis of Scrap Tires in a Continuous Rotary Kiln Reactor," *Industrial Engineering Chemistry Research,* vol. 43, no. 17, pp. 5133-5145, 2004.

[28] S. Murugan, M. Ramaswamy and G. Nagarajan, "The Use of Tyre Pyrolysis Oil in Diesel Engine," *waste Management,* vol. 28, no. 12, p. 2743–2749, 2008.

[29] M. Banar, V. Alkyildiz, A. Ozkan, Z. Cokaygil and O. Onay, "Characterization of Pyrolytic Oil Obtained from Pyrolysis of TDF (Tire Derived Fuel)," *Energy Conservation & Management,* vol. 62, pp. 22-30, 2012.

[30] M. R. Islam, H. Haniu and M. R. Alam Beg, "Liquid Fuels and Chemicals from Pyrolysis of Motorcycle Tire Waste:Product Yields, Compositions and Related Properties," *Fuel,* vol. 87, no. 13-14, p. 3112–3122, 2008.

[31] I. A. Alzubaidy, Y. M. Ali, M. Alsuwaidi, R. Alsheikh, A. Attari, F. Leher, A. Raghad, T. Ozkul and K. Zraqi, "Kinetics of Novel Adsorption Desulfurization Techniques for Diesel Fuel Using Different Sorbents," in *International Conference on Chemical, Medical and Environmental Issues*, Dubai, 2013.

[32] A. Vosough, A. Noghrehabadi, M. Ghalambaz and S. Vosough, "Exergy Concept and its Characteristic," *International Journal of Multidisciplinary Science and Engineering,* vol. 2, no. 4, 2011.

[33] A. Hepbasli, "A Key Review on Exergetic Analysis and Assessment of Renewable Energy Resources for a Sustainable Future," *Renewable and Sustainable Energy Reviews,* vol. 12, no. 3, pp. 593-661, 2008.

[34] S. de Oliveira Junior, Exergy : Production, Cost and Renewability, New York: Springer, 2013.

[35] V. Karamarkovic, M. Marasevic, R. Karamarkovic and M. Karamarkovic, "Recuperator for Waste Heat Recovery from Rotary Kilns," *Applied Thermal Engineering,* vol. 54, no. 2, pp. 470-480, 2013.

[36] M. Prins and K. Ptasinski, "Energy and Exergy Analysis of the Oxidation and Gasification of Carbon," *Energy,* vol. 30, no. 7, pp. 981-1002, 2005.

[37] T. Seager and T. Thies, "A Uniform Definition and Quantitative Basis for Industrial Ecology," *Journal of Cleaner Production,* vol. 10, no. 3, pp. 225-235, 2002.

[38] C. J. Koroneos, G. Roumbas and N. Moussiopoulos, "Exergy Analysis of Cement Production," *International Journal of Exergy,* vol. 2, no. 1, pp. 55-68, 2005.

[39] G. Tsatsaronis, "Thermoeconomic Analysis and Optimization of Energy Systems," *Progress in Energy and Combustion Science,* vol. 19, no. 3, pp. 227-257, 1993.

[40] J. Szargut, D. R. Morris and F. R. Steward, Exergy Analysis of Thermal, Chemical, and Metallurgical Processes, New York: Hemisphere Publishing, 1988.

[41] J. F. Peters, F. Petrakopoulou and J. Dufour, "Exergetic Analysis of a Fast Pyrolysis Process for Bio-Oil Production," *Fuel Processing Technology,* vol. 119, pp. 245-255, 2014.

[42] A. A. Boateng, C. A. Mullen, L. Osgood-Jacobs, P. Carlson and N. Macken, "Mass Balance, Energy, and Exergy Analysis of Bio-Oil Production by Fast Pyrolysis," *Journal of Energy Resources Technology,* vol. 134, no. 4, 2012.

[43] R. A. Z. Vigouroux, B. F. Medina, I. H. Moya, A. Rubio and O. Cruz, "Exergetic Evaluation of Pyrolysis Process of Dichrostachys Cinerea," in *16th European Biomass Conference and Exhibition*, Valencia, 2008.

[44] K. Wang, R. F. Sun and G. P. Zhang, "Energy Efficiency Assessment and Exergy Analysis for Lignite Pyrolysis Process System," *Advanced Materials Research,* pp. 1184-1188, June 2014.

[45] Y. Tanaka, M. Tamura and Y. Nakamura, "Exergy Evaluation of the Municipal Solid Waste Incinerator Systems Using Natural Gas," Toho Gas Co., Ltd., Najoya.

[46] H. Baumann and A. M. Tillman, The Hitch Hicker's Guide to LCA, Sweden: Studentlitteratur, 2012.

[47] H. Baumann, Life Cycle Assessment and Decision Making :Theories and Practices, Gothenburg: Chalmers University of Technology, 1998.

[48] K. Simonen, Life Cycle Assessment, New York: Routledge, 2014.

[49] M. Goedkoop, M. Oele, J. Leijting, T. Ponsioen and E. Meijer, "Introduction to LCA with SimaPro," PRe Consultants, Amersfoort, 2013.

[50] J. Guinee, Life Cycle Assessment: An Operational Guide to the ISO Standards, Dordrecht: Centrum Milieukunde Leiden, 2002.

[51] ISO 14044 Environmental Management :Life Cycle Assessment :Requirements and Guidelines, Geneva: International Standards Organization, 2006.

[52] General Guide for Life Cycle Assessment: Detailed Guidance: International Reference Life Cycle Data System Handbook, Luxembourg: European Commission Joint Research Centre Institute for Environmental and Sustainability, 2010.

[53] ISO 14025 Environmental Labels and Declarations : Principles and Procedures, Geneva: International Standards Organization, 2006.

[54] M. Z. Hauschild, M. Goedkoop, J. Guinee, R. Heijungs, M. Huijbergts, O. Jollliet, M. Margni, A. D. Schryver, S. Humbert, A. Laurent, S. Sala and R. Pant, "Identifying Best Existing Practice for Characterization Modeling in Life Cycle Impact Assessment," *International Journal of Life Cycle Assessment,* vol. 18, pp. 683-697, 2012.

[55] Z. Zhong, B. Song and M. Zaki, "Life Cycle Assessment to Flash Pyrolysis of Wood Waste," *Journal of Cleaner Production,* vol. 18, no. 12, pp. 1177-1183, 2010.

[56] P. Steele, M. E. Puettmann, V. K. Penmetsa and J. E. Cooper, "Life-Cycle Assessment of Pyrolysis Bio-Oil Production," *Forest Products Journal,* vol. 62, p. 326–334, 2012.

[57] H. Wang, L. Wang and A. Shahbazi, "Life Cycle Assessment of Fast Pyrolysis of Municipal Solid Waste in North Carolina of USA," *Journal of Cleaner Production,* vol. 87, pp. 511-519, 2015.

[58] S. Grierson, V. Strezov and J. Bengtsson, "Life Cycle Assessment of a Microalgae Biomass Cultivation, Bio-Oil Extraction and Pyrolysis Processing Regime," *Algal Research,* vol. 2, no. 3, p. 299–311, 2013.

[59] A. Corti and L. Lombardi, "End Life Tyres: Alternative Final Disposal Processes Compared by LCA," *Energy,* vol. 29, no. 12-15, pp. 2089-2108, 2004.

[60] H. H. Khoo, "Life Cycle Impact Assessment of Various Waste Conversion Technologies," *Waste Management,* vol. 29, no. 6, p. 1892–1900, 2009.

[61] S. Evangelisti, C. Tagliaferri, R. Clift, P. Lettieri, R. Taylor and C. Chapman, "Life Cycle Assessment of Conventional and Two-Stage Advanced Energy-from-Waste Technologies for Municipal Solid Waste Treatment," *Journal of Cleaner Production,* vol. 100, pp. 1-12, 2015.

[62] F. Emun, M. Gadalla, T. Majozi and D. Boer, "Integrated Gasification Combined Cycle (IGCC) Process Simulation and Optimization," *Computers and Chemical Engineering,* vol. 34, no. 3, pp. 331-338, 2010.

[63] N. Ramzan, A. Ashraf, S. Naveed and A. Malik, "Simulation of Hybrid Biomass Gasification Using Aspen Plus: A comparative Performance Analysis for Food, Municipal Solid and Poultry Waste," *Biomass and Bioenergy,* vol. 35, no. 9, pp. 3962-3969, 2011.

[64] A. Donatelli, P. Iovane and A. Molino, "High Energy Syngas Production by Waste Tyres Steam Gasification in a Rotary Kiln Pilot Plant. Experimental and Numerical Investigations," *Fuel,* vol. 89, no. 10, pp. 2721-2728, 2010.

[65] M. Bajus and N. Olahova, "Thermal Conversion of Scrap Tyres," *Petroleum and Coal,* vol. 53, no. 2, pp. 98-105, 2011.

[66] J. F. Peters, D. Iribarren and J. Dufour, "Predictive Pyrolysis Process Modelling in Aspen Plus," in *European Biomass Conference and Exhibition*, Copenhagen, 2013.

[67] Z. Sogut, Z. Oktay and H. Karakoc, "Mathematical Modeling of Heat Recovery from a Rotary Kiln," *Applied Thermal Engineering,* vol. 30, no. 8-9, pp. 817-825, 2010.

[68] C. J. Koroneos, G. Roumbas and N. Moussiopoulos, "Exergy Analysis of Cement Production," *International Journal of Exergy,* vol. 2, no. 1, pp. 55-68, 2005.

[69] P. Saneipoor, G. Naterer and I. Dincer, "Heat Recovery from a Cement Plant with a Marnoch Heat Engine," *Applied Thermal Engineering,* vol. 31, no. 10, pp. 1734-1743, 2011.

[70] A. S. Gutierrez, J. B. C. Martinez and C. Vandecasteele, "Energy and Exergy Assessments of a Lime Shaft Kiln," *Applied Thermal Engineering,* vol. 51, no. 1-2, pp. 273-280, 2013.

[71] S. Spyrakis, K. D. Panopoulos and E. Kakaras, "Synthesis, Modeling and Exergy Analysis of Atmospheric Air Blown Biomass Gasification for Fischer-Tropsch Process," *International Journal of Thermodynamics,* vol. 12, pp. 187-192, 2009.

[72] C. Sreejith, C. Muraleedharan and P. Arun, "Energy and Exergy Analysis of Steam Gasification of Biomass Materials: A Comparative Study," *International Journal of Ambient Energy,* vol. 34, no. 1, pp. 35-52, 2012.

[73] V. Silva and A. Rouboa, "Using a Two -Stage Equilibrium Model to Simulate Oxygen Air Enriched Gasification of Pipe Biomass Residues," *Fuel Processing Technology,* vol. 109, pp. 111-117, 2013.

[74] Y. Wang, K. Yoshikawa, T. Namioka and Y. Hashimoto, "Performance Optimization of Two-Staged Gasification System for Wood Biomass," *Fuel Processing Technology,* vol. 88, no. 3, pp. 243-250, 2007.

[75] "DGEngineering.de,"DG Engineering group.Available: http://www.DGEngineering.de. [Accessed 15 March 2015].

[76] PRé, "SimaPro Database Manual Methods library," PRé Consultants, San Francisco, 2014.

[77] H. Szoege, "Environmental Impact of Rail and Road Transport," *Economic and Environmental Studies,* vol. 11, no. 4, pp. 405-421, 2011.

[78] R. H. Perry, Perry's Chemical Engineering Handbook, New York: McGraw Hill, 1997.

[79] A. Vatani, M. Mehrpooya and F. Gharagheizi, "Prediction of Standard Enthalpy of Formation by a QSPR Model," *International Journal of Molecular Sciences,* vol. 8, pp. 407-432, 2007.

[80] M. V. Roux, M. Temprado, J. S. Chickos and Y. Nagano, "Critically Evaluated Thermochemical Properties of Polycyclic Aromatic Hydrocarbons," *Journal of Physical and Chemical Reference Data,* vol. 37, 2008.

[81] M. J. Monte, S. P. Pinto, A. I. L. Ferreira, L. M. Amaral, V. L. Freitas and D. M. Ribeiro da Silva, "Fluorene: An Extended Experimental Thermodynamic Study," *The Journal of Chemical Thermodynamics,* vol. 45, no. 1, p. 53–58, 2012.

[82] O. Ignatenko, A. Schaik and M. Reuter, "Exergy as a Tool for Evaluation of the Resource Efficiency of Recycling Systems," *Minerals Engineering,* vol. 20, no. 9, p. 862–874, 2007.

[83] V. Karamarkovic, M. Marasevic, R. Karamarkovic and M. Karamarkovic, "Recuperator for Waste Heat Recovery from Rotary Kilns," *Applied Thermal Engineering,* vol. 54, pp. 470-480, 2013.

[84] S. Li, Q. Yao, Y. Chi and K. Cen, "Pilot Scale Pyrolysis of Scrap Tires in a Continuous Rotary Kiln Reactor," *Industrial Engineering Chemistry Research,* vol. 43, no. 17, pp. 5133-5145, 2004.

[85] K. L. Lee, K. Y. Cheung, K. L. Lam and C. W. Hui, "Optimization of Multi-Stage Waste Tyre Pyrolysis Process," in *European Symposium on Computer Aided Process Engineering*, Italy, 2010.

[86] T. Kotas, The Exergy Method of Thermal Plant Analysis, Malabar: Krieger Publishing Company, 1995.

[87] R. Ayers, L. Ayers and K. Martinas, "Eco-Thermodynamics:Exergy and Life Cycle Analysis," INSEAD, Fontainebleau, 1996.

[88] G. Wall, Exergetics, bucaramanga: Exergy Ecology Democracy, 2009.

[89] F. Karaca, "Chemical Exergy Calculations for Petroleum and Petroleum-Derived Liquid Fractions," *International Journal of Exergy,* vol. 12, no. 4, pp. 451 - 462, 2013.

[90] A. Masini and R. U. Ayres, An Application of Exergy Accounting to Four Basic Industries, Fontainebleau: INSEAD, 1996.

[91] L. Stougie, "Exergy and Sustainability: Insights Into the Value of Exergy Analysis in Sustainability Assessment of Technological Systems," Zutphen, 2014.

[92] "chemea,"Available: http://www.chemea.com. [Accessed 15 march 2015].

[93] "Hnbjhb Company," Alibaba Group, Available: http://www.hunbjhb.en.alibaba.com. [Accessed 10 March 2015].

[94] "google.ae," Google Inc,. Available: http://www.google.ae/maps. [Accessed 20 March 2015].

[95] "sunrise-econergy.en," Shenzhen sunrise-econergy Co., Available: http://www.sunrise-econergy.en.alibaba.com. [Accessed 20 March 2015].

[96] "happyzebra,"Available:http://www.happyzebra.com/distance-calculator/UAE-Shenzhen. [Accessed 21 March 2015].

[97] Thsljx Company, Available: www.thsljx.en.alibaba.com. [Accessed 14 March 2015].

[98] A. Bridgwater, Progress in Thermochemical Biomass Conversion, London: John Wiley and Sons, 2001.

[99] V. Karamarkovic, M. Marasavic and R. Karamakovic, "Recuperator for Waste Heat Recovery from Rotary Kilns," *Applied Thermal Engineering,* vol. 54, pp. 470-480, 2013.

Appendix A

Table A.1 Product compositions from pyrolysis simulation model at different temperatures (w/w)

Component	400 ^{o}C	450 ^{o}C	500 ^{o}C	550 ^{o}C
Water	0.2387	0.2329	0.225	0.2129
Carbon dioxide	0.032	0.0353	0.0372	0.0369
Carbon monoxide	0.0016	0.0047	0.0122	0.0273
Hydrogen sulfide	0.0562	0.056	0.0557	0.0551
Nitric oxide	2.98E-24	4.27E-19	2.45E-21	3.69E-20
Nitric dioxide	8.18E-40	6.85E-34	1.80E-35	1.01E-33
Methane	0.6623	0.6619	0.6608	0.6587
Ethane	1E-05	2E-05	2E-05	3E-05
Propane	1E-09	2E-09	3E-09	5E-09
Ethylene	4E-09	2E-08	8E-08	3E-07
Propylene	7E-12	3E-11	1E-10	5E-10
1-Butene	5E-16	3E-15	2E-14	7E-14
N-Butane	9E-14	2E-13	4E-13	7E-13
N-Pentane	6E-18	2E-17	4E-17	9E-17
2-Methyl-2-Butene	5E-19	3E-18	1E-17	5E-17
3-Methyl-2-Pentene	4E-22	1E-21	4E-21	9E-21
2,3-Dimethyl-1-Butene	4E-23	3E-22	2E-21	8E-21
Isobutane	7E-14	1E-13	3E-13	4E-13
Trans-2-Butene	9E-16	5E-15	2E-14	9E-14
Isobutylene	2E-15	1E-14	4E-14	2E-13
1,3-Butediene	3E-18	5E-17	6E-16	5E-15
Trans-2-Pentene	1E-19	9E-19	5E-18	2E-17
Cis-2-Butene	7E-16	4E-15	2E-14	7E-14
1-Pentene	4E-20	3E-19	2E-18	8E-18
2-Methyl-1-Butene	2E-19	1E-18	7E-18	3E-17
2-Methyl-1,3 butadiene	1E-21	2E-20	3E-19	2E-18
N-Decane	-	-	-	-
N-Undecane	-	-	-	-
N-Dodecane	-	-	-	-

Component	400 °C	450 °C	500 °C	550 °C
N-Tridecane	-	-	-	-
N-Tetradecane	-	-	-	-
N-Pentadecane	-	-	-	-
N-Hexadecane	-	-	-	-
N-Heptadecane	-	-	-	-
N-Octadecane	-	-	-	-
N-Nonadecane	-	-	-	-
N-Eicosane	-	-	-	-
N-Heneicosane	-	-	-	-
N-Docosane	-	-	-	-
N-Tetracosane	-	-	-	-
N-Pentacosane	-	-	-	-
N-Hexacosane	-	-	-	-
N-Nonacosane	-	-	-	-
N-Triacontane	-	-	-	-
N-Dotriacontane	-	-	-	-
Naphthalene	-	-	-	-
Acenaphthene	-	-	-	-
Fluorene	-	-	-	-
Phenanthrene	-	-	-	-
Pyrene	-	-	-	-
Chrysene	-	-	-	-
Anthracene	-	-	-	
Benzene	3E-17	3E-16	2E-15	1E-14
Toluene	6E-20	6.72E-19	5.67E-18	3.65E-17
Ethyl benzene	1.35E-20	5.08E-23	5.26E-22	4.07E-21
O-Xylene	4.23E-20	1.39E-22	1.28E-21	8.93E-21
M-Xylene	9.12E-20	2.88E-22	2.56E-21	1.73E-20
P-Xylene	3.66E-20	1.16E-22	1.04E-21	7.08E-21
Styrene	2.15E-26	8.57E-25	2.11E-23	3.48E-22

Component	600 ºC	650 ºC	700 ºC	750 ºC
Water	0.1948	0.1701	0.1405	0.1103
Carbon dioxide	0.0337	0.0277	0.0202	0.0131
Carbon monoxide	0.0532	0.0906	0.1356	0.1809
Hydrogen sulfide	0.0543	0.0531	0.0517	0.0502
Nitric oxide	3.90E-19	3.00E-18	1.74E-17	7.94E-17
Nitric dioxide	3.27E-32	6.50E-31	8.27E-30	7.12E-29
Methane	0.6551	0.6498	0.6435	0.6371
Ethane	4E-05	4E-05	5E-05	6E-05
Propane	7E-09	1E-08	1E-08	2E-08
Ethylene	8E-07	2E-06	4E-06	9E-06
Propylene	1E-09	4E-09	9E-09	2E-08
1-Butene	3E-13	8E-13	2E-12	5E-12
N-Butane	1E-12	2E-12	3E-12	4E-12
N-Pentane	2E-16	3E-16	5E-16	9E-16
2-Methyl-2-Butene	2E-16	5E-16	1E-15	3E-15
3-Methyl-2-Pentene	2E-20	4E-20	8E-20	1E-19
2,3-Dimethyl-1-Butene	3E-20	1E-19	4E-19	1E-18
Isobutane	7E-13	1E-12	2E-12	2E-12
Trans-2-Butene	3E-13	8E-13	2E-12	4E-12
Isobutylene	5E-13	1E-12	3E-12	7E-12
1,3-Butediene	3E-14	2E-13	8E-13	3E-12
Trans-2-Pentene	8E-17	3E-16	7E-16	2E-15
Cis-2-Butene	2E-13	6E-13	2E-12	4E-12
1-Pentene	3E-17	1E-16	4E-16	1E-15
2-Methyl-1-Butene	1E-16	3E-16	9E-16	2E-15
2-Methyl-1,3 butadiene	2E-17	9E-17	4E-16	2E-15
N-Decane	-	-	-	-
N-Undecane	-	-	-	-
N-Dodecane	-	-	-	-
N-Tridecane	-	-	-	-
N-Tetradecane	-	-	-	-

Table A.1 (Continued)

Component	600 °C	650 °C	700 °C	750 °C
N-Pentadecane	-	-	-	-
N-Hexadecane	-	-	-	-
N-Heptadecane	-	-	-	-
N-Octadecane	-	-	-	-
N-Nonadecane	-	-	-	-
N-Eicosane	-	-	-	-
N-Heneicosane	-	-	-	-
N-Docosane	-	-	-	-
N-Tetracosane	-	-	-	-
N-Pentacosane	-	-	-	-
N-Hexacosane	-	-	-	-
N-Nonacosane	-	-	-	-
N-Triacontane	-	-	-	-
N-Dotriacontane	-	-	-	-
Naphthalene	-	-	-	-
Acenaphthene	-	-	-	-
Fluorene	-	-	-	-
Phenanthrene	-	-	-	-
Pyrene	-	-	-	-
Chrysene	-	-	-	-
Anthracene	-	-	-	-
Benzene	7E-14	3E-13	1E-12	3E-12
Toluene	1.88E-16	8.03E-16	2.91E-15	9.19E-15
Ethyl benzene	2.46E-20	1.21E-19	5.02E-19	1.79E-18
O-Xylene	4.93E-20	2.24E-19	8.16E-19	2.85E-18
M-Xylene	9.30E-20	4.11E-19	1.54E-18	5.00E-18
P-Xylene	3.82E-20	1.70E-19	6.38E-19	2.08E-18
Styrene	4.12E-21	3.67E-20	2.58E-19	1.48E-18

Component	800 ºC	850 ºC	900 ºC
Water	0.0834	0.0619	0.0458
Carbon dioxide	0.0079	0.0045	0.0025
Carbon monoxide	0.22	0.2504	0.2724
Hydrogen sulfide	0.0489	0.0479	0.0472
Nitric oxide	2.95E-16	9.35E-16	2.61E-15
Nitric dioxide	4.45E-28	2.16E-27	8.62E-27
Methane	0.6316	0.6274	0.6243
Ethane	7E-05	8E-05	9E-05
Propane	2E-08	3E-08	3E-08
Ethylene	2E-05	3E-05	6E-05
Propylene	4E-08	8E-08	1E-07
1-Butene	1E-11	2E-11	5E-11
N-Butane	6E-12	8E-12	1E-11
N-Pentane	1E-15	2E-15	3E-15
2-Methyl-2-Butene	7E-15	1E-14	3E-14
3-Methyl-2-Pentene	2E-19	4E-19	6E-19
2,3-Dimethyl-1-Butene	2E-18	6E-18	1E-17
Isobutane	3E-12	4E-12	5E-12
Trans-2-Butene	9E-12	2E-11	3E-11
Isobutylene	1E-11	3E-11	5E-11
1,3-Butediene	1E-11	3E-11	8E-11
Trans-2-Pentene	4E-15	9E-15	2E-14
Cis-2-Butene	8E-12	2E-11	3E-11
1-Pentene	2E-15	6E-15	1E-14
2-Methyl-1-Butene	5E-15	1E-14	2E-14
2-Methyl-1,3 butadiene	6E-15	2E-14	5E-14
N-Decane	-	-	-
N-Undecane	-	-	-
N-Dodecane	-	-	-
N-Tridecane	-	-	-
N-Tetradecane	-	-	-

Component	800 °C	850 °C	900 °C
N-Pentadecane	-	-	-
N-Hexadecane	-	-	-
N-Heptadecane	-	-	-
N-Octadecane	-	-	-
N-Nonadecane	-	-	-
N-Eicosane	-	-	-
N-Heneicosane	-	-	-
N-Docosane	-	-	-
N-Tetracosane	-	-	-
N-Pentacosane	-	-	-
N-Hexacosane	-	-	-
N-Nonacosane	-	-	-
N-Triacontane	-	-	-
N-Dotriacontane	-	-	-
Naphthalene	-	-	-
Acenaphthene	-	-	-
Fluorene	-	-	-
Phenanthrene	-	-	-
Pyrene	-	-	-
Chrysene	-	-	-
Anthracene	-	-	-
Benzene	9E-12	2E-11	5E-11
Toluene	2.58E-14	6.53E-14	1.51E-13
Ethyl benzene	5.58E-18	1.56E-17	3.93E-17
O-Xylene	8.36E-18	2.20E-17	5.28E-17
M-Xylene	1.44E-17	3.73E-17	8.78E-17
P-Xylene	6.02E-18	1.56E-17	3.69E-17
Styrene	7.08E-18	2.91E-17	1.04E-16

Appendix B

Table B.1 Compositions of components in gaseous products [28, 65]

Component	Composition (wt. %)
1-Butene	1.80E+00
1,3 Butadine	4.00E-01
n-pentane	1.2
1-pentene	0.01
Benzene	5.00E-01
Naphthalene	2.23E+00
Fluorene	4.20E-01
H_2S	2.10E-01
CO_2	6.50E+00
Methylpropylene	6.00E-01
CO	4.74E+01
n-decane	1.74E-04
Trans-2-pentene	1.00E-01
Cis-2-butene	3.00E-01
2-Methyl-2-butene	2.00E-01
2-Methyl-1-butene	3.00E-02
Isoprene	4.00E-02
n-Nonacosane	1.41E-04
n-Triacontane	2.01E-05
n-Dotraiacontane	5.33E-05
Phenanthrene	1.90E-01
Anthracene	7.10E-01
Fluoranthene	4.70E-01
Pyrene	7.00E-01
Chrysene	5.50E-01
H_2O	2.50E-01
Ethane	6.70E+00
Ethene	4.50E+00
Propane	5.70E+00
Propene	7.80E+00
n-butane	1.4
trans-2-butene	0.3
Methane	9.3
n-undecane	2.50E-04
n-dodecane	2.41E-04
n-tridecane	2.64E-04
n-tetradecane	3.01E-04
n-pentadecane	7.47E-04

Component	Composition (wt. %)
n-heptadecane	8.20E-04
n-octadecane	2.40E-04
n-nonadecane	1.43E-04
n-eicosane	1.28E-04
n-heneicosane	1.15E-04
n-docosane	1.07E-04
n-tetracosane	1.19E-04
n-pentacosane	1.32E-04
n-hexacosane	1.12E-04
n-hexadecane	3.45E-04

Table B.2 Heat capacities and molecular weights of components [78] *

Compound	A	B	C	D
1-Butene	24.915	2.06E-01	5.98E-05	-1.42E-07
1,3 Butadine	18.835	2.04E-01	6.25E-05	-1.71E-07
n-pentane	-3.626	0.4873	-2.58E-04	5.31E-08
1-pentene	2.691	3.98E-02	-1.24E-05	0
Benzene	-33.92	4.74E-01	-3.02E-04	7.13E-08
Naphthalene	67.099	4.32E-02	9.17E-04	-1.00E-06
Fluorene	27.408	1.29E-02	7.07E-06	-1.63E-08
H_2S	3.931	1.49E-03	0	0
N_2	31.15	-1.36E-02	2.68E-05	-1.17E-08
CO_2	0.818205	9.97E-04	-7.61E-07	2.80E-10
Methylpropylene	6.772	3.14E-01	-1.03E-04	-3.68E-08
CO	1.03	1.27E-04	2.41E-07	-2.17E-10
n-decane	31.78	7.45E-01	-1.10E-04	-2.27E-07

$$C_P(J/_{mol.K})^* = A + BT + CT^2 + DT^3$$

Component	Heat Capacity (J/kg.K)	Source
Trans-2-pentene	2.952	[79]
Cis-2-butene	2.93	[78]
2-Methyl-2-butene	2.392	
2-Methyl-1-butene	2.996	
Isoprene	3.088	
n-Nonacosane	3.379	[79]
n-Triacontane	3.696	
n-Dotraiacontane	3.536	
Phenanthrene	2.121	[80]
Anthracene	2.172	
Fluoranthene	2.15	
Pyrene	2.094	
Chrysene	2.148	
H_2O	2.097	[78]
Ethane	3.362	
Ethene	2.827	
Propane	3.235	
Propene	2.83	
n-butane	3.218	
trans-2-butene	2.919	
Methane	7.368	
n-undecane	3.187	
n-dodecane	3.182	
n-tridecane	3.178	
n-tetradecane	3.177	
n-pentadecane	3.174	
n-hexadecane	3.172	
n-heptadecane	3.17	
n-octadecane	3.17	
n-nonadecane	3.167	
n-eicosane	3.166	
n-heneicosane	3.326	[79]
n-docosane	3.334	
n-tetracosane	3.348	
n-pentacosane	3.354	
n-hexacosane	3.361	

Table B.3 Components molecular weight and standard heat of formation

Component	Molecular Weight (g/mol)	ΔH_f (J /mol)	Source
1-Butene	56.11	-5.40E+05	[78]
1,3 Butadine	54.09	1.09E+08	
n-pentane	72.15	-1.47E+08	
1-pentene	70.13	-2.13E+07	
Benzene	78.11	8.29E+07	
Naphthalene	128.17	15.058	
Fluorene	166	191.9	[81]
H_2S	34.08	-2.06E+07	[78]
N_2	14.01	0	
CO_2	44.91	-3.94E+05	
Methylpropylene	56.11	-1.70E+07	
CO	28.01	-1.11E+08	
n-decane	142	-2.49E+08	
Trans-2-pentene	70.13	-111.09	[79]
Cis-2-butene	56.1	-7.40E+06	[78]
2-Methyl-2-butene	70.13	-4.18E+07	
2-Methyl-1-butene	70.13	-3.53E+07	
Isoprene	68.12	75.73	[82]
n-Nonacosane	408.79	-782.85	[79]
n-Triacontane	422.81	-809.72	
n-Dotraiacontane	450.87	-863.47	
Phenanthrene	178.23	202.2	[80]
Anthracene	178.23	229.4	
Fluoranthene	202.26	291.4	
Pyrene	202.25	225.5	
Chrysene	228.29	268.7	
H_2O	18.02	-2.42E+08	[78]
Ethane	30.07	-8.38E+07	
Ethene	28.05	5.25E+07	
Propane	44.096	-1.05E+08	
Propene	42.079	1.97E+07	
n-butane	58.12	-1.26E+08	
trans-2-butene	56.11	-1.10E+07	
Methane	16.04	-7.45E+07	

Table B.3 (Continued)

Component	Molecular Weight (g/mol)	ΔH_f (J /mol)	Source
n-undecane	156	-2.70E+08	[78]
n-dodecane	170	-2.91E+08	
n-tridecane	184	-3.12E+08	
n-tetradecane	198	-3.32E+08	
n-pentadecane	212	-3.53E+08	
n-hexadecane	226	-3.74E+08	
n-heptadecane	240	-3.94E+08	
n-octadecane	255	-4.15E+08	
n-nonadecane	269	-4.36E+08	
n-eicosane	283	-4.56E+08	
n-heneicosane	297	-567.85	[79]
n-docosane	311	-594.73	
n-tetracosane	339	-648.48	
n-pentacosane	353	-675.35	
n-hexacosane	367	-702.23	

Table B.4 Ultimate analysis and physical properties of char and heavy fuel oil

Material	Physical Property		Ultimate Analysis (wt. %)	
Heavy Fuel Oil [83]	LHV	40410 kJ/kg	C	84.58
	Specific Heat Capacity	1.717 kJ/kg.K	H	11.10
	Density	853 kg/m^3	N+O	0.60
			S	0.72
			W	3.00
Char [84]	Calorific Value	31.5 MJ/kg	C	82.17
			H	2.28
			N	0.61
			S	2.32
Tire [85]	Specific Heat Capacity	1.23kJ/kg.K		

Table B.5 Standard chemical exergy of compounds

Compound	$\bar{e}^0_{ch}$ (kJ/kg)	Source
1-Butene	47568.97	[86]
1,3 Butadine	2791.56	[87]
n-pentane	48191.96	[86]
1-pentene	47201.81	[87]
Benzene	42383.05	[86]
Naphthalene	41071.78	
Fluorene	-	
H_2S	23613.52	[86]
N_2	51.40	
CO_2	8993.32	
Methylpropylene	47401.532	[88]
CO	9819.71	[87]
n-decane	47400	[86]
Trans-2-pentene	988.12	
Cis-2-butene	1.19E+03	[87]
2-Methyl-2-butene	851.23	
2-Methyl-1-butene	925.37	
Isoprene	18671.46	[82]
n-Nonacosane	89106.57	
n-Triacontane	89087.65	[89]
n-Dotraiacontane	82824.85	
Phenanthrene	40407.34	[87]
Anthracene	40563.32	
Fluoranthene	39229	[90]
Pyrene	1616.91	[89]
Chrysene	41000	[91]
H_2O	6607.83	
Ethane	50028.59	
Ethene	48477.94	[86]
Propane	49056.38	
Propene	47786.46	
n-butane	48501.89	
trans-2-butene	1142.44	[87]
Methane	52141.74	
n-undecane	4.74E+04	
n-dodecane	4.73E+04	[86]
n-tridecane	4.73E+04	
n-tetradecane	4.72E+04	
n-pentadecane	4.72E+04	[86]
n-hexadecane	4.72E+04	

Table B.5 (Continued)

Compound	$\bar{e}^0_{ch}$ (kJ/kg)	Source
n-heptadecane	4.70E+04	[86]
n-octadecane	2.63E+02	[87]
n-nonadecane	4.70E+04	[86]
n-heneicosane	4.70E+04	[89]
n-docosane	4.70E+04	
n-tetracosane	8.92E+04	
n-pentacosane	8.92E+04	
n-hexacosane	8.92E+04	
O_2	124800	[86]

Table B.6 Gibbs free energy and chemical exergy of components

Component	ΔG(kJ/mol)	Source
CO_2	-394.64	[78]
H_2O	-237.35	
O_2	0	
n-Nonacosane	2748.11	[92]
n-triacontane	2840.9	
n-dotraiacontane	218.56	
n-tetracosane	2284.18	
n-pentacosane	2376.97	
n-hexacosane	2469.75	

Appendix C

C.1 Capital Goods Specifications

C.1.1 Pyrolysis plant [93]**.** The plant was brought from Hunan, China to Sharjah with the following distance:

5659 nautical miles sea + 1212 km land [94].

Weight of Plant = 45 ton

Distance travelled in tonneskilometers = (45 ton *(10480.5 km sea + 1212 km land)

= 54540 tkm sea + 471622.5 tkm land

C.1.2 Balloon gas storage [95]**.** The balloon was brought from Shenzhen, China to Sharjah with the following distance:

5786 nautical miles sea + 126 km land [96].

Weight of Balloon = 1.53 ton

Distance travelled in tonneskilometers = (1.53 ton*(10715.7 km sea + 126 km land)

= 16395.02 tkm sea +192.78 tkm land

C.1.3 Tire pretreatment equipment [97]**.** The steel wire separator, the ring cutter, the strip cutter, and the rim cutter were brought from Hunan, China to Sharjah with the following distance:

= 10480.5 tkm sea + 1212 tkm land

Weight of steel wire separator = 1.1 ton

Weight of ring cutter = 0.5 ton

Weight of strips cutter = 0.9 ton

Weight of rim cutter = 0.8 ton

Distance travelled in tonneskilometers = 3.3 ton * (10480.5 km sea + 1212 km land)

=34585.65 tkm sea + 3999.6 tkm land

C.2 Raw Materials Specifications

      C.2.1 Waste tire transportation. The waste tires were brought from a solid waste dumping area to the plant in the industrial area, Sharjah with the distance:

= 31.9 km land [94]

Weight of the Tires (functional unit) = 1 kg

Distance travelled in tonneskilometers = 1 kg* 31.9 km = 0.0319 tkm

      C.2.2 Heavy oil transportation. The heavy oil was brought from a local company in Sharjah to the plant with the distance:

= 6.5 km land [94]

Weight of the Oil (on the basis of 1 kg WT) = 219.36 kg

However, after shredding WT = 0.81 kg, then the Heavy oil needed = 177.68 kg

Distance travelled in tonneskilometers = 177.68 kg*6.5 km = 1.155 tkm

C.3 Product Distribution Calculations

      C.3.1 Pyrolytic oil transportation. The pyrolytic oil was assumed to have been transported to the cement factory in Sharjah with the distance:

= 6.6 km land [94]

Weight of the pyrolytic oil = 0.36531 kg

Distance travelled in tonnekilometers = 0.36531 kg* 6.6 = 0.00241 tkm

      C.3.2 Char transportation. The char was assumed to have been transported to a carbon black factory in Sharjah with the distance:

= 30.9 km land [94]

Weight of the char = 0.33453 kg

Distance travelled in tonneskilometers = 0.33453 kg* 30.9 km = 0.0103 tkm

      C.3.3 Steel transportation. The steel was assumed to have been transported to a steel trading company in Sharjah with the distance:

= 69.7 km land [94]

Weight of the steel = 0.19 kg

Distance travelled in tonneskilometers = 0.19 kg * 69.7 km = 0.0132 tkm

C.4 Electricity Calculations

C.4.1 WT pretreatment electricity [97].The capacity of the steel wire separator is 1100 kg/hr of WT with power needed around 11 kW, based on 1 kg WT:

$= 11 \text{ kJs}^{-1}*(3600\text{s})/1100 \text{ kg} = 36 \text{ kJ} = 0.036 \text{ MJ}$

The capacity of the ring cutter is 500 kg/hr of WT with a power needed around 3 kW, based on 1 kg WT:

$= 3 \text{ kJs}^{-1}*(3600\text{s})/500 \text{ kg} = 21.6 \text{ kJ} = 0.0216 \text{ MJ}$

The capacity of the strips cutter is 900 kg/hr of WT with a power needed around 4 kW, based on 1 kg WT:

$= 4 \text{ kJs}^{-1}*(3600\text{s})/900 \text{ kg} = 16 \text{ kJ} = 0.016 \text{ MJ}$

The capacity of the rim cutter is 800 kg/hr of WT with a power needed around 7.5 kW, based on 1 kg WT:

$= 7.5 \text{ kJs}^{-1}*(3600\text{s})/800 \text{ kg} = 33.75 \text{ kJ} = 0.03375 \text{ MJ}$

C.4.2 Pyrolysis reactor electricity [93]**.** The capacity of the pyrolysis reactor is 10 ton/day of WT with power needed around 19 kW; the power is needed for the WT feeding, char removal and pyrolytic oil recovery.

$= 19 \text{ kJs}^{-1}*(24*3600\text{s})/10000 \text{ kg} = 164.16 \text{ kJ} = 0.1642 \text{ MJ}$

C.5 Emissions of the Combustion Process Calculations [98]

C.5.1 Combustion of pyrolytic oil. CO amount = 4.6 mg/MJ = 4.6 *42.66 MJ/kg = 196.24 mg/kg

Where 42.66 MJ/kg is the GCV of the pyrolytic oil.

For 0.36531 kg of pyrolytic oil:

CO emission = 7.169E-5 kg

NOx amount = 88 mg/MJ = 88*42.66 MJ/kg = 3754.08 mg/kg

For 0.36531 kg of pyrolytic oil:

NOx emission =1.3714E-3 kg

Soot amount = 2.4 bac = 2.4 g/kg oil

For 0.36531 kg of pyrolytic oil:

Soot emission = 8.767E-4 kg

Particulate amount = 86 mg/MJ =3668.76 mg/kg

For 0.36531 kg of pyrolytic oil:

Particulate emission = 1.34E-3 kg

C.5.2 Combustion of heavy fuel oil. CO amount = 4.6 mg/MJ = 4.6 *40.41 MJ/kg = 185.89 mg/kg

Where 40.41 MJ/kg is the GCV of the heavy fuel oil [99].

For 177.68 kg of heavy fuel oil:

CO emission = 0.033 kg

NOx amount = 88 mg/MJ = 88*40.41 MJ/kg = 3556.08 mg/kg

For 177.68 kg of heavy fuel oil:

NOx emission =0.632 kg

Soot amount = 2.4 bac = 2.4 g/kg oil

For 177.68 kg of heavy fuel oil:

Soot emission = 0.426 kg

Particulate amount = 86 mg/MJ =3475.26 mg/kg

For 177.68 kg of heavy fuel oil:

Particulate emission = 0.617 kg.

C.5.3 Combustion of non-condensable gases. CO amount = 4.6 mg/MJ = 4.6 *33.203 MJ/kg = 152.73 mg/kg

Where 33.203 MJ/kg is the GCV of the NCG

For 228.3 kg of NCG:

CO emission = 0.0349 kg

NOx amount = 88 mg/MJ = 88*33.203 MJ/kg = 2921.86 mg/kg

For 228.3 kg of NCG:

NOx emission =0.667 kg

Soot amount = 2.4 bac = 2.4 g/kg $_{NCG}$

For 228.3 kg of NCG:

Soot emission = 0.548 kg

Particulate amount = 86 mg/MJ =2855.46 mg/kg

For 228.3 kg of NCG:

Particulate emission = 0.652 kg

C.6 Calculation for the Sensitivity Analysis

To calculate the amount of heat that will be generated from the combustion of non-condensable gases the data needed are illustrated in table C.1. It is based on 1 kg of WT.

The CV then will be 33.203 MJ/kg$_{NCG}$. From the energy balance around the pyrolysis reactor (based on 1 kg of WT), the amount of NCG needed is 281.85 kg. After WT shredding the amount of WT will be 0.81 kg.

Then the amount of NCG needed for pyrolysis is 228.3 kg.

Then, the energy produced in the combustion of NCG:

= 33.203 MJ/kg$_{NCG}$* 228.3 kg = 7.58 GJ.

Table C.1 Densities of the components in Non-condensable Gases

Component	Density (kg/m^3) [78]	Composition [65]	Mixture Density (kg/m^3)
CO_2	1.977	6.50E-02	1.28E-01
H_2S	1.997	2.10E-03	4.19E-03
CO	1.145	4.74E-01	5.43E-01
Ethane	1.3562	6.70E-02	9.09E-02
Ethene	1.178	4.50E-02	5.30E-02
Propane	2.0098	5.70E-02	1.15E-01
Propene	1.81	7.80E-02	1.41E-01
n-butane	2.48	1.40E-02	3.47E-02
trans-2-butene	4.217	3.00E-03	1.26E-02
Methane	0.656	9.00E-03	5.90E-03
1-Butene	2.6748	1.80E-02	4.81E-02
1,3 Butadine	2.55	4.00E-03	1.02E-02
Methylpropylene	3.1	6.00E-03	1.86E-02
Trans-2-pentene	-	9.99E-04	-
Cis-2-butene	4.283	3.00E-03	1.28E-02
2-Methyl-2-butene	3.425	2.00E-03	6.84E-03
n-pentane	3.178	1.20E-02	3.81E-02
1-pentene	3.392	1.00E-04	3.39E-04
Benzene	3.828	5.00E-03	1.91E-02
2-Methyl-1-butene	3.425	3.00E-04	1.03E-03
Total (kg/m^3)			1.28E+00

Vita

Ryan K. Altayeb was born in 1988 in Omdurman, Sudan. She received her elementary education in a public school in Saudi Arabia and graduated from a secondary school as one of the top hundred in Sudan. Then, she joined the University of Khartoum, Sudan, in November 2005. She attained her Bachelor of Science in Chemical Engineering, with honors, in September 2010.

She worked for one year as a teaching assistant at the University of Khartoum in 2011 and another year as a research assistant at Africa City of Technology, Sudan in 2012. In February 2013, Eng. Ryan began the Master's program in Chemical Engineering at the American University of Sharjah, UAE, where she received a scholarship as a graduate teaching assistant.