

A Comparative Review of Waste Tyre Pyrolysis, Gasification and Liquefaction (PGL) Processes

Edison Muzenda

Abstract—This article reviews remedial waste tyre technologies as well as utilization for energy and material recovery. Application examples and scenarios are drawn from developing countries such as South Africa. Waste minimization and utilization technologies are required to address the growing waste tyre problem. Waste tyres cause a variety of environmental and health challenges as they are bulk and non-degradable. Potential solutions to address the waste tyre problem are pyrolysis, gasification and liquefaction (PGL) processes. Process conditions and potential products for each process are reviewed and discussed in this paper. An environmental impact assessment of PGL processes and potential remedial solutions are also presented. PGL processes have huge potential for business. However the success of any operation depends on several economic and environmental factors such as capital and operating costs, feed availability, permitting process and emission from these operations.

Keywords— Economic, Energy, Environmental, Gasification, Liquefaction, Pyrolysis, Minimization, Waste

I. INTRODUCTION

WASTE tyres are a significant part of the urban waste stream that is growing in quantity [1]. Waste tyres are non-degradable due to the vulcanization process they undergo during their production. The vulcanized rubber is cross-linked with sulphur bonds and is further protected by antioxidants and antiozonants [2]. In 1998, the world production and sales of tyres were estimated to have passed the one billion mark, with 2007 estimates reported at 1.3 billion tyres [1]. In South Africa, 60 to 100 million waste tyres are estimated to be abandoned lying across the country. Another 11 million or so are added to the stockpile each year as vehicle owners by new ones. Many of these scrap tyres end up in landfills while others are burnt for heat or left in the open. Combustion of tyres produces toxic gases, which contain carcinogenic and mutagenic chemicals [3], [4]. Thus waste tyre incineration requires expensive air emissions control systems and there is also concern about the levels of ash produced. Attempts on waste tyre reuse as solid fuel are largely documented. Waste tyres have been used as principal or secondary fuel sources in the production of steam, electricity, cement, lime, paper, steel and into the incineration of garbage; however these

experiences have been severely limited by the small market demand and the overall operational costs of these plants [5]. It is well known that tyres possess high volatile and low ash contents with a heating value greater than that of coal and biomass. These properties make them ideal materials for thermal processes like pyrolysis, gasification and liquefaction [6]-[8]. In 2012, the South African Department of Environmental Affairs, reacted to the potential danger and hazard to the environment caused by waste tyres by demanding that the tyre industry be the first in South Africa to develop an industry waste management plan. The plan which became effective in 2013 is driven by the Recycling and Economic Development Initiative of South Africa (REDISA). [9] The initiative had collected about 28 800 tonnes of old tyres by June 2014 [9]. This shows a challenge in the management of waste tyres as about 240,000 tonnes of new tyres enter the market every year in South Africa [9]. The plan relies on independent transporters delivering old tyres to regional storage depots from where they are passed on to recyclers [9]. Although REDISA is making significant contribution, a huge market for waste tyres is required to address this growing environmental challenge. Pyrolysis, gasification, and liquefaction are technologies that could be used to divert a significant portion of the scrap tyres currently being landfilled.

TABLE I
COMPOSITION OF WHOLE TYRES

Rubber	38%
Fillers (Carbon black, silica, carbon chalk)	30%
Reinforcing material (steel, rayon, nylon)	16%
Plasticizers (oils and resins)	10%
Vulcanisation agents (Sulphur, zinc oxide, various chemicals)	4%
Antioxidants to counter ozone effect and material fatigue	1%
Miscellaneous	1%
Elementary Composition	
Carbon	86.40%
Hydrogen	8.00%
Nitrogen	0.50%
Sulphur	1.70%
Oxygen	2.40%
Proximate Analysis	
Volatiles	62.10%
Fixed carbon	29.40%
Ash	7.10%
Moisture	1.30%

II. PYROLYSIS, GASIFICATION AND LIQUEFACTION (PGL) PROCESSES

PGL processes present alternative routes for the disposal of scrap tyres. They are currently used for the conversion of carbonaceous materials to fuels and other valuable products,

Edison Muzenda is a Professor of Chemical Engineering. Department of Chemical Engineering, Faculty of Engineering and the Built Environment, University of Johannesburg, Doornfontein, P O Box 17011, 2028, South Africa (Email: emuzenda@uj.ac.za).

and their contribution may become significant as the supply of natural resources get depleted.

A. Pyrolysis

Pyrolysis is an endothermic process that induces the thermal decomposition of feed materials without the addition of any reactive gases, such as air or oxygen. The thermal efficiency of this process is approximately 70%, and can increase to 90% with the use of pyrolytic products as fuel [10]. The use of tyre chips instead of whole tyres may also increase the efficiency of the process by 20-30% [10]. Some of the problems related to the process are the high cost of the plant and residue treatment [11]. The thermal energy used to drive the pyrolysis reaction is applied indirectly by thermal conduction through the walls of the containment reactor. Pyrolysis generally occurs at temperatures between 400 and 800°C [12]. As the temperature changes, the product distribution (or the phase of the product) are also altered. Lower pyrolysis temperatures usually produce more liquid products while higher temperatures favour the production of gases. The speed of the process and rate of heat transfer also influences the product distribution. Slow pyrolysis (carbonization) can be used to maximize the yield of solid char. This process requires a slow pyrolytic decomposition at low temperatures. Rapid quenching is often used to maximize the production of liquid products, by condensing the gaseous molecules into liquid. In some pyrolysis processes, 80% liquid product yield can be achieved [13]. Steam can also be used as a reaction medium, allowing pyrolysis to occur at lower temperatures and higher pressures. The use of water as a process medium also allows the feedstock to be introduced into the reactor in an aqueous form. An additional advantage of water or steam is that the resulting char has a relatively high surface area and porosity that is similar in nature to activated charcoal. Nitrogen gas can be supplied to maintain the inert atmosphere in the reactor and also to sweep away the produced vapour to the condensers. Furthermore, purging the system with nitrogen helps to minimize secondary reactions in the hot zone. Some of the problems related to the process are the high cost of the plant and residue treatment [11]. Fig. 1 shows the schematic flow diagram for a pyrolysis process. Pyrolytic oil (a mixture of paraffins, olefins, and aromatic compounds) have been reported to have a high gross calorific value (GCV) of about 41–44 MJ/kg and this makes them potential replacements for conventional liquid fuels. In addition it abundantly contains olefins, especially limonene and light aromatics, which have higher market values as chemical feedstock [13]. The gaseous product has gross calorific values between 30 and 40 MJ Nm⁻³ and this is sufficient to meet the process plant energy requirements [3]. Several studies have reported the production of char and activated carbons from waste tyres and their successful applications as adsorbents for various pollutants [3]. Table VII shows the summarized PGL process operating conditions and products.

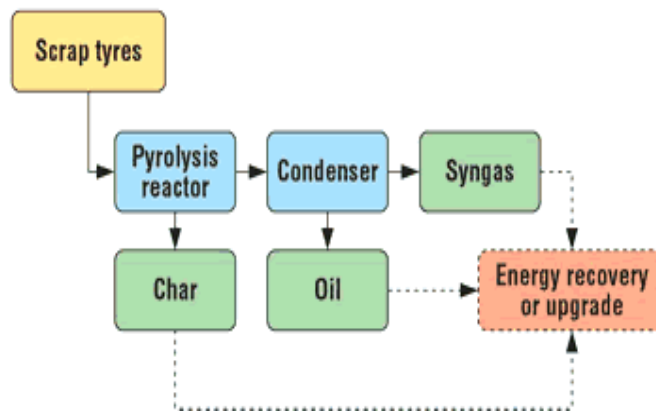


Fig. 1. Pyrolysis process pathway

B. Gasification

Gasification is a sub-stoichiometric oxidation of organic material and a typical process is shown in Fig. 2. The thermochemical process for gasification is more reactive than pyrolysis. Gasification is generally carried out at higher temperatures (700-1400°C) than pyrolysis and liquefaction and in the presence of a partially oxidative reactive atmosphere [14]. It involves the use of air, oxygen (O₂), hydrogen (H₂), or steam/water as a reaction agent. The energy efficiency of the gasification process is reported to be around 76% [15]. Depending on the gasification process, the de-volatilization step can take place in a separate reactor upstream of the gasification reaction, in the same reactor, or simultaneously with the gasification reaction. The gasification process can include a number of different chemical reactions, depending on the process conditions and the gasification agent. Equations 1 to 8 show gasification reactions for carbonaceous char.



The oxygen requirement for the partial oxidation process can be supplied by air, oxygen enriched air, or pure oxygen at a range of pressures. The oxygen delivery method influences the cost and efficiency of the process. The gas calorific value can be improved from relatively low values of 4 to 10MJ/m³ using low-cost, air-blown partial oxidation driven gasifiers, to values of 10 to 15 MJ/m³ for oxygen-blown processes and 25 to 30 MJ/m³ for hydrogen-blown processes, which compares well with natural gas at 39MJ/m³.

The gasification of waste tyres is an attractive utilization route as the gaseous products can be stored, transported and can be easily fed to existing boilers and combustors with little modifications [16], [17]. Steam gasification of waste tyres has the potential of producing quality syngas. However, conventional gasification systems require high temperatures to decompose the feed stock and reforming reactions which influence the overall efficiency of the process [18].

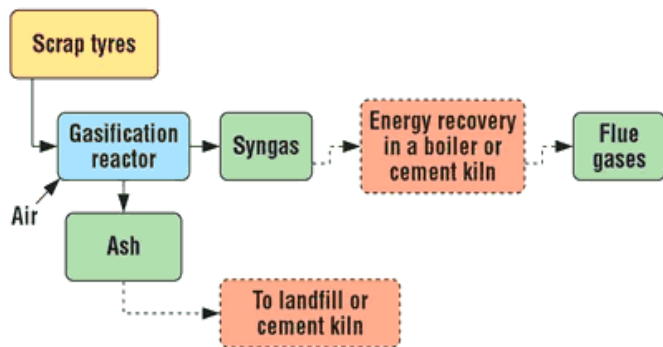


Fig. 2 Gasification process pathway

C. Liquefaction

Liquefaction is the thermochemical conversion of an organic solid into petroleum like liquid. Liquefaction typically involves the production of a liquid composed of heavy molecular compounds with properties similar, but not identical, to those of petroleum based fuels. The mechanisms involved in waste tyre liquefaction process are diffusion of solvent into the rubber; rubber swelling; rubber degradation; rubber dissolution; product separation from insoluble [19]. The gases and condensates are regarded as important by-products of waste tyre liquefaction. The gases start to evolve at around 200°C. The rate of gas generation reaches maximum when the mixture is at optimum reaction temperature. Condensate generation follows a similar pattern to gases and is composed of hydrocarbons ranging from C₆ to C₂₀ [20]. An oil yield of up to 90.2% is possible [20]. Tyres could be liquefied singly, or in combination with other waste materials and/or coal in co-processing schemes, in one or two stage processes. Liquefaction provides an effective approach for converting the organic content into oils.

III. PRODUCT YIELD

The pyrolysis process yields, oil, non-condensable gases, solids mainly carbon, metal and other inert material. In contrast, gasification is a more reactive thermal process that utilizes air, oxygen, hydrogen, or steam. Gasification happens at a higher temperature range than pyrolysis with products being mainly gaseous. Liquefaction happens at a lower temperature range compared to both pyrolysis and gasification and produces mainly liquid products.

A. Fractional gas yield

Table II shows the PGL product gaseous composition. The PGL gases are mainly composed of hydrocarbons together with some CO_x (CO, CO₂), H₂S as well as heavier hydrocarbons (C₄>C₄). Table III shows high carbon and hydrogen contents for pyrolysis and gasification. Table IV shows the fractional gaseous yields for pyrolysis and gasification. Pyrolysis produce lesser gaseous fractions due to the condensation of lighter gases.

TABLE II
PGL GAS CONSTITUENTS

Pyrolysis [12]	Gasification [20]	Liquefaction [19]
H ₂ S	H ₂	H ₂
CO	CO	CO
CO ₂	CO ₂	CO ₂
CH ₄	CH ₄	Alkanes
Alkanes	Ethane	Alkenes
alkenes	Ethylene	H ₂ S (trace)
	Acetylene	

TABLE III
PGL GAS ULTIMATE ANALYSIS

Element	Pyrolysis [12]	Gasification [20]
C (wt%)	85.8	60.2
H ₂ (wt%)	14.2	22.5
O ₂ (wt%)	trace	17.4
GHV (MJ/kg)	44.6	50.2

B. Fractional liquid yield

Increasing the reaction temperature decreases oil yields for PGL processes due to continuous thermal cracking and vapour decomposition into permanent gases. Pyrolysis oil can be sub categorized into light oil (C₃+C₈), diesel oil (C₈+C₁₈), fuel oil (C₁₈+C₃₀), and residual oil (C₃₀), Table V, [20]. Gasification produces minimum oil due to thermal cracking and steam reforming reactions at high temperatures which result in the major extensions of secondary cracking reactions into the gases [21].

C. Fractional char yield

For PGL processes, char yield decreases with increasing temperature due to the non-volatilization of the fixed carbon, Table IV.

TABLE IV
PYROLYSIS AND GASIFICATION GAS YIELD

Pyrolysis [13]			Gasification [21]	
Reaction Temp °C	Tyre gas wt%	Tyre gas wt%	Reaction Temp °C	Tyre gas wt%
450	4.5	6.8	850	34.7
500	5.5	8.0	925	64.5
600	8.9	8.1	1000	85.9

TABLE V
PGL FRACTIONAL OIL YIELD

Pyrolysis [13]			Gasification [21]		Liquefaction [20]	
Reaction Temp, °C	Tyre Oil, wt%	Tyre Oil, wt%	Reaction Temp, °C	Tyre Oil, wt%	Reaction Temp, °C	Tyre Oil, wt%
450	58.1	28.3	850	27.0	320	67.4
500	56.2	41.1	925	21.8	370	90.2
600	53.1	39.4	1000	5.3	380	83.7

TABLE VI
PGL FRACTIONAL CHAR YIELD

Pyrolysis [13]			Gasification [21]		Liquefaction [20]	
Reaction Temp, °C	Tyre Oil, wt%	Tyre Oil, wt%	Reaction Temp, °C	Tyre Oil, wt%	Reaction Temp, °C	Tyre Oil, wt%
450	37.4	53.4	850	43.4	320	24.1
500	38.3	44.1	925	38.5	370	4.7
600	38.0	44.5	1000	33.3	380	2.3

TABLE VII
PGL PROCESS SUMMARY

Process	Liquefaction	Gasification	Pyrolysis
Process definition	Liquefaction is the thermochemical conversion of an organic solid into liquids.	Gasification is a sub-stoichiometric oxidation of organic material to maximize waste conversion to high temperature flue gases, mainly CO ₂ and H ₂ .	The thermal degradation of carbonaceous material in an oxygen deprived atmosphere to maximize thermal decomposition of solid into gases and condensed liquid and residual char.
Operating conditions:			
Reaction environment	Oxidizing (oxidant amount larger than that required by stoichiometric combustion)	Reducing (oxidant amount lower than that required by stoichiometric combustion)	Total absence of any oxidant
Reactant gas	none	Air, pure oxygen, oxygen enriched air, steam	None
Temperature	Between 300°C and 450°C [19]	Between 550 – 900 °C [20] (in air)	Between 400 and 800°C [3]
Pressure	Atmospheric	Atmospheric	Slightly above atmospheric pressure
Process output:			
Produced gases	H ₂ , CO, CO ₂ , Alkanes Alkenes, H ₂ S (trace)	CO, H ₂ , CO ₂ , H ₂ O, CH ₄	CO, H ₂ , CH ₄ and other hydrocarbons
Produced liquids	Petroleum like liquid, heavy molecular compounds with properties similar to those of petroleum based fuels.	Condensable fraction of tar and soot which is minimal.	Oil is similar to diesel and can be used as a fuel. High aromatic content, thus can serve as a feed stock in the chemical industry
Produced solids		After the combustion process. Bottom ash is often produced as vitreous slag that can be utilized as backfilling material for road construction.	The pyrolysis char residue has a considerable amount of carbon content and can either be utilized as tyre derived fuel for the process or be sold as a carbon-rich material for the manufacture of activated carbon or for other similar industrial purposes
Pollutants	SO _x , NO _x , CO,	H ₂ S, HCl, CO, NH ₃ , HCN, tar, alkali, particulate.	H ₂ S, HCl, NH ₃ , HCN, tar, particulate.

IV. ENVIRONMENTAL IMPACT ASSESSMENT

This section presents an evaluation of the environmental impacts of waste tyre pyrolysis including potential mitigation measures. These impacts include air emissions, liquid wastes, and solid residues. Generally, the environmental impacts are similar in all three PGL technologies. When compared to operations that utilize combustion of waste tyres, it is generally accepted that PGL technologies yield equal or lower environmental risks in most cases. However, the information available is limited, due to the small number of full-scale PGL facilities [22]. Exhaust gas clean-up of PGL processes is less compared to incineration, however, proper design and operation of the process and emissions control systems are necessary to ensure that all health and safety requirements are met. The control of air emissions is made less costly and complex for PGL processes compared to incineration because (a) subsequent combustion of low-molecular-weight gases from pyrolysis and gasification processes produces much cleaner air compared to the combustion of raw feed stocks (b) pyrolysis and gasification processes use zero or minimum air or oxygen. (c) Pyrolytic gases are typically in a reducing environment, and can be treated or utilized unlike the fully combusted (oxidative) exhaust.

A. Air Emissions

Air emissions may be the greatest environmental concern in PGL operations using waste tyres. The gases from pyrolysis and gasification processes (and subsequent combustion processes, if applicable) can contain a variety of air pollutants that must be controlled prior to discharge into the ambient air. These include particulate matter (PM), oxides of nitrogen (NO_x), oxides of sulphur (SO_x), dioxins and furans, hydrocarbon (HC) gases, metals, carbon dioxide (CO₂), and carbon monoxide (CO) [21]. There are many strategies available for controlling emissions from waste tyre thermal processes depending on the process requirements and facility size.

There are a number of different emission control strategies that can be applied in PGL processes. An example of a mid-process air pollution control system is the Thermostelect® process, a high-temperature conversion technology. The company currently has four facilities in commercial operation worldwide, with three others under construction [22]. The Thermostelect® process is capable of processing different waste streams, including tyres. The Thermostelect® process uses gasification for primary processing, but can also be applicable to high temperature pyrolysis. After completion of the gasification/ pyrolysis

stage, the synthesis gas exits the reaction chamber and flows into a water jet quench where it is instantaneously cooled to below 95°C. The rapid cooling prevents the formation of dioxins and furans by dramatically reducing the residence time of the synthesis gas at high temperature. Entrained particles (such as elemental carbon and mineral dusts), heavy metals, chlorine (in the form of hydrochloric acid (HCL)), and fluorine (in the form of HF) are also separated out in the quench. The quench water is maintained at a pH of 2 to ensure that heavy metals are dissolved as chlorinated and fluorinated species, enabling washing from crude synthesis gas. Following the quench process, the synthesis gas flows into a demister and then into alkaline scrubbers, where the remaining particulates and HCl/HF droplets are removed. Then the gas passes through a desulfurization scrubber for the removal of hydrogen sulphide (H₂S) by direct conversion into elemental sulphur. The scrubber is a packed bed that is sprayed with scrubbing liquor consisting of water and a dissolved Fe-III chelate that oxidizes the H₂S to elemental sulphur and water. Finally, the gas is dried in a counter current packed bed scrubber using triethylene glycol liquor. The fully cleaned synthesis gas can then be conveyed to engines, boilers, or turbines for electricity production. Alternatively, the gas can be converted to higher molecular weight fuels such as diesel fuel. Other control systems such as the Exxon thermal de-NO_x system for NO_x emissions, fabric filters for particulate matter and wet scrubbers for SO_x emissions can be utilized.

B. Liquid Residues

The primary liquid products from tyre PGL processes are pyrolysis oils and any residual scrubber solutions from the air pollution control equipment. Pyrolysis oils from tyres and other products are complex mixtures of hydrocarbons. The liquid fraction can contain a range of species including acids, alcohols, aldehydes, aromatics, ketones, esters, heterocyclic derivatives, and phenols, along with varying amounts of water [23]. These oils typically contain a number of substances that can be considered toxic, but can be handled safely by using certain industrial practices. They also represent an intermediate product that is not disposed of, but can be used either via combustion for energy production or for the production of other chemicals after upgrading. Residual products from the gas cleaning and water recovery processes can be handled using well-established procedures. These residual products include industrial-grade salts and a separate precipitate containing the heavy metals from the feedstock stream. In some cases, this precipitate may be rich enough in zinc and lead to warrant recovery in smelter operations [22].

C. Solid Residues

The solid residue remaining from PGL processes is typically an inorganic ash or char. The inorganic ash is the residue from the 3 to 5% of inorganic material in the tyre that cannot be converted to energy or products through PGL [22]. The ash contains non-volatile trace metals that are more concentrated in the ash than in the feedstock, but with proper management

can be treated and disposed of in a manner that does not pose an environmental threat. In some cases, metals can be recycled from the ash. The leach-ability of the ash is used to indicate whether the ash is classified as a hazardous or non-hazardous waste. Char contains carbon black; sulphur; zinc oxide; clay fillers; calcium and magnesium carbonates and silicates, all of which produce PM₁₀ emissions. Operations such as screening, grinding and processing cause PM₁₀ emissions and could be controlled with dust collectors and a baghouse filters. If markets for the char cannot be developed, the char becomes a major solid waste problem. In addition, to landfill disposal, plastic bags should be used and must be shipped and disposed of in steel drums to prevent additional fugitive emissions during transportation and disposal [24].

V. CONCLUSION

PGL processes can be applied in the treatment of waste tyres for energy and material recovery. The success of each facility is influenced by the economics, feedstock requirements and availability, and the permitting processes. The paper also evaluated the environmental impacts of waste tyre pyrolysis and the potential mitigation measures.

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REFERENCES

- [1] A. Quek and R. Balasubramanian, "Liquefaction of waste tires by pyrolysis for oil and chemical: A review," *Journal of Analytical and Applied Pyrolysis*, vol. 101, pp. 1-16, 2013.
- [2] M. Beecham, "Global market review of automotive tyres: Forecast to 2014," Aroq Limited, United Kingdom JA1867566, 31 Jul 2008.
- [3] California Integrated Waste Management Board, "Effects of Waste Tires, Waste Tire Facilities, and Waste Tire Projects on the Environment," California Integrated Waste Management Board 432-96-029, Apr 1996.
- [4] United States Environmental Protection Agency. (2014, 03 Jun). *Scrap Tires*. Available: <http://www.epa.gov/osw/conservematerials/tires/basic.htm>
- [5] V. K. Sharma, "Disposal of waste tyres for energy recovery and safe environment: A review," *Energy Conversion and Management*, vol. 39, pp. 511-528, 1998.
- [6] A. V. Bridgwater, "Renewable fuels and chemicals by thermal processing of biomass," *Chemical Engineering Journal*, vol. 91, pp. 87-102, 2003.
- [7] N. Kiran, E. Ekinici, and C. E. Snape, "Recycling of plastic wastes via pyrolysis," *Resource Conservation and Recycling*, vol. 29, pp. 273-283, 2000.
- [8] M. Morris and L. Waldheim, "Energy recovery from solid waste fuels using advanced gasification technology," *Waste Management*, vol. 18, pp. 557-564, 1998.
- [9] D. Furlonger, "Tyre recycling sets off on road to environmental sustainability," *Business Day Live*, 18 August 2014.
- [10] R. M. Islam, "Innovation in pyrolysis technology for management of scrap tire: A solution of energy and environment.," *International Journal of Environmental Science and Development*, vol. 1, pp. 89-96, 2010.
- [11] S. Burger. (2012) Environmental protection: False start. *Engineering News*.

- [12] J. Bester, D. Kruger, and A. Hinks, *Recycling and reuse of waste tyres in South Africa, in used/post consumer tyres*. London: Thomas Telford Publishings, 2004.
- [13] F. M. Laresgoiti, "Chromatographic analysis of the gases obtained in tyre pyrolysis," *Journal of Analytical and Applied Pyrolysis*, vol. 55, pp. 43-54, 2000.
- [14] D. Pradhan, "Recovery of value added fuels from waste polyolefins/ bicycle tyre and tube," Master's, Department of Chemical Engineering, National Institute of Technology Rourkela, 2011.
- [15] H. J. Manuel and W. Dierkes, "Expert overviews covering the science and technology of rubber and plastics," Rapra Technology Limited 1997.
- [16] V. Belgiorno, "Energy from Gasification of Solid Wastes " *Waste Management*, vol. 23, pp. 1-15, 2003.
- [17] A. Franco and N. Giannini, "Perspectives for the use of biomass as fuel in combined cycle power plants," *International Journal of Thermal Science*, vol. 44, pp. 163-177, 2005.
- [18] S. Portofino, "Optimizing H₂ production from waste tyres via combined steam gasification and catalytic reforming," *Energy and Fuels*, vol. 25, pp. 2232-2241, 2011.
- [19] J. M. Bouvier and M. Gelus, "Rubber Chemical Technology," *Resource Conservation and Recycling*, vol. 59, p. 12, 1986.
- [20] S. O. Myongsook, "Scrap Tire Liquefaction: Effect of Reaction Time and Temperature," Master's, Department of Chemical Engineering, Hong-Kong University, Hong-Kong, 2010.
- [21] S. Portofino, "Steam gasification of waste tyre: Influence of process temperature on yield and product composition," *Waste Management*, vol. 33, pp. 672-678, 2013.
- [22] L. K. Hunt and R. R. Kovalak, "Devulcanization of Cured Rubber," United State of America Patent, 1999.
- [23] EPA, "Tire-Derived Fuel; Wastes, Resource Conservation, Common Wastes & Materials, Scrap Tires," United State of America 2012.
- [24] P. M. Bhatt and P. D. Patel, "Suitability of Tyre Pyrolysis Oil (TPO) as an Alternative Fuel for Internal Combustion Engine," *International Journal of Advanced Engineering Research and Studies*, pp. 61-65, 2012.