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Developments in waste tyre thermochemical conversion processes: gasification, pyrolysis and liquefaction

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Fossil fuels, particularly crude oil, have proven to be a source of energy to households, transportation and power industries over the past decades. This natural reserve is diminishing at an alarming rate with crude oil having reserves to last the earth for the next half a century. As a result, researchers are constantly seeking remedial technologies to close this gap. Thermochemical conversion processes such as pyrolysis, gasification and liquefaction (PGL) offer an alternative solution to mitigating the world's high reliance on crude oil. These processes can be employed to provide energy, fuel and high-end value-added products. This paper aims to highlight all the research and development advancements and trends that have been made over the past three decades while employing waste tyres and other feedstock. In addition, the prominent countries and their associated researchers who have made novel discoveries in the field of thermochemical conversion are extensively discussed. The research findings show that significant research outputs such as the utilization of vast types of feed materials, the reaction mechanisms, the factors affecting the processes, and the application of the different end-products for thermochemical processes are well documented in the literature. Also, the collected data showed that significant advancements have been achieved in developing PGL technologies. The following conclusions were drawn: (i) PGL technologies show a generally increasing percentage interest from 1990 to 2020, (ii) many authors have identified the end-products obtained from waste feedstocks, such as; waste tyres, biomass, plastics, food waste, microalgae and animal manure to yield promising application benefits, (iii) China has shown the greatest interest in investing into waste to energy initiatives and has demonstrated the vast applications of waste derived products and, (iv) employing waste tyres as a feedstock has shown potential for producing high-end value products in their crude form or refined form. Some of the shortcomings identified during the study are the modest interest shown by most African regions as well as the lack of regulatory frameworks developed by certain countries.

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1. Introduction

The discovery of fossil fuel has led to the world's high dependency on crude oil as a source of fuel. Statistics show that crude oil contributes 35% of the total energy consumption, in 2005 the total worldwide daily consumption stood at over 84 million barrels per day (bbl per d) and this was forecast to be 90 million and 120 million bbl per d for 2016 and 2030 respectively.[1] Records show that in 2019, 100.74 million bbl per d of crude oil[2] were consumed globally, this equates to approximately 5 barrels of oil per person annually when considering the 2020 global population of 7713 billion.[3] Energy security is a global concern with the world's natural reserves rapidly diminishing and prices constantly rising. The crude oil supply is also affected by factors such as political instabilities and infrastructure challenges in different regions. As of late, the recently discovered COVID-19 virus, which has become a global pandemic, has significantly affected worldwide economies including the price of crude oil. The benchmarked United States of America (USA) oil price deteriorated to below $0.00 and the international Brent crude oil fall by nearly 70% during April of 2020.[4] The South African petrol price fall by as much as R3.82 in early 2020, from R15.84 in January 2020 to R12.02 in May 2020.[5] The sharp decline in prices is attributed to fuel oversupply while a low fuel demand was experienced because of the imposed travel restrictions and economic lockdowns. Moreover, the oil price was already being affected by Saudi Arabia and Russia price war, as a result, this phenomenon further impaired the global oil prices.[6] Other non-conventional sources of oil such as shale oil and sand oil have

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Table 1 A comparison of the prices of crude oil and TDTO from 2011–2021

Year	Crude oil price (US $ bbl per d)[31]	Trye derived oil price US $
2011	96.91	
2012	97.03	
2013	100.28	0.43 L^{-1} (ref. 32)
2014	94.96	0.52 L^{-1} (ref. 33)
2015	54.14	
2016	45.97	0.26 kg^{-1}[a] (ref. 34)
2017	52.74	
2018	68.04	
2019	59.60	3.50 L^{-1} (ref. 28)
2020	42.84	0.844 L^{-1} (ref. 35)
2021 (January)	54.41	

[a] Kilograms (kg).

been under exploration globally for the past decades, with China over the past 70 years developing and extracting oil from shale oil to be directly utilized as fuel.[7] Their limited use has been attributed to the high ash content and lesser aromatic hydrocarbon production from shale oil,[8] while sand oil showed small concentrations of hydrocarbons (less than 1%) and a high presence of tailings comprising of an amalgamation of fine clay and sand.[9]

Since the early 90s, researchers have been embarking on research and development of thermochemical conversion processes that will play a critical role in alleviating the energy supply deficiency. The novelty in these processes is that different material feedstocks, commonly coal,[10–12] including waste products such as waste tyres,[12–14] biomass;[15–17] plastics;[18–20] food waste;[21–23] microalgae;[24] and animal manure[25] *etc.* can be employed to yield high-end final products. However, waste tyres will be the core feedstock of discussion in this publication. Waste tyres fall under the general waste category. Their landfilling disposal has been banned in the majority of first world countries such as European Union member states, the USA *etc.* and third world countries such as South Africa. This has presented a major challenge as waste tyres pose environmental and health risks to the ecosystem. According to Yadav (2020), approximately 3 billion tyres are presently produced all over the world.[26–28] The USA alone reached tyre production rates of 313 million annually, China, Japan, India and South Africa have significantly produced annual tyres production figures of 239 million (2004),[27] 97 million (2017),[29] 80 million (2010)[27] and, 16 million (2015)[30] respectively. Consequently, many of these developed and developing countries have considered the employment of waste tyres in thermochemical processes to yield high-end value products, while simultaneously addressing their waste accumulation challenges. A comparison of the crude oil price bbl per d over the past decade with the price of tyre derived treated pyrolysis oil (TDTO) obtained from work done by several authors is highlighted in Table 1. It can be deduced from Table 1 that the highest average oil price which stood at US $100.28 bbl per d was obtained in 2013. This phenomenon was attributed to the substantial decline in Libyans oil production rates accompanied by concerns of instability in other countries, this propelled crude oil prices to rise above US $100. When comparing the prices of the two commodities in 2013, the price of crude oil stood at US $0.63 L^{-1}, however, Ning *et al.*, reported a cost effective selling price of US $0.43 L^{-1} which proved to be 32% more economical than the price of crude oil. Conversely, in 2020 the average price of crude oil was reported to be US $0.27 L^{-1} while Nkosi *et al.*, reported a higher TDTO selling price of US $0.84 L^{-1}. This excessive price is attributed to the global COVID-19 pandemic, which plummeted oil prices significantly, as highlighted previously. As at January 2021 the average crude oil price stands at US $0.34 L^{-1}, indicating a steady increase overtime.

Thermochemical processing can be defined as the use of high-temperature conditions to promote the chemical conversion of carbonaceous material under different reaction conditions into energy and a variety of chemical products in different phases.

For instance, thermal degradation methods such: incineration, combustion, and PGL technologies currently exist, with gasification and pyrolysis proving to be more practically applicable and economically sound.[36] Incineration and combustion have limitations as they require strict toxic gas mitigation steps and the processes do not yield products of economic and practical value.[37,38] Various process parameters such as reactor configuration, temperature, pressure, heating rate, retention time, reactive or inert environment, expulsion gas flow rate, use of catalyst *etc.* can be employed to optimize the system and/or the quality of derived products.

Thermochemical conversion research has focused on the production of gaseous, liquid and solid intermediates and subsequently their advancement into fuel and other products. The different processes have the potential of producing a variety of value-added products.[39] The gaseous fraction produces a gas that is a suitable fuel for electricity production. Depending on the thermochemical process applied, the gas can be further refined to produce transportation fuels through the Fischer–Trosph process. Hydrogen (H_2) can be yielded through the water gas shift reaction, methanol and dimethyl ether can also be produced.[40]

Pyrolytic gas produced from waste rubbers has a calorific value range of 29.9–42.1 MJ m^{-3} (ref. 41) and is abundant in alkanes; alkenes; aromatics; acids, and sulphides,[42] with aliphatic compounds (chain alkenes and cyclic alkenes), and aromatics (toluene, xylene, styrene) being the most dominant by 70% and 13.1% respectively.[43] The presence of alkenes, cyclohexenes, and aromatics is attributed to the tyres's decomposition of natural rubber. The liquid fraction yielded during the pyrolysis and liquefaction processes have several noteworthy industrial and domestic uses. The oil is an assortment of hydrocarbons comprising of C_6–C_3 linear paraffins with C_8–C_{13} being the most dominant, and with low concentrations of alkene (non-condensed alkenes, pentenes, pentadienes, and isoprene) and aromatics (naphthenes, terpenes, limonene, BTX and, benzopyrenes).[41] Oliveira Neto *et al.* observed a directly

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proportional relationship between temperature and the production of aromatic compounds. This can be attributed to the further interactions between the aliphatic and aromatics compounds, as well as and the cyclic formation of aliphatic series.[28] In crude form, the pyrolytic oil can be used as a combustion fuel[44] for various industrial machineries such as boilers, kilns and furnaces[45] and in the road construction industry as asphalt or bitumen. This application has proven to contribute significantly to the diverting of waste tyres away from landfills as no prior treatment of the waste material is required. Pyrolytic oil has been found to reach an energy value of 44 MJ kg^{-1}.[41] Yousefi *et al.*[46] prepared polymer-improved asphalt using recycled polyethylene and waste tyre-derived oil. Improvements in the performance of the asphalt were achieved at a low range and high temperatures. Upon further refining, pyrolytic oil can be employed as an alternative for transportation fuel or as a diesel blend,[29,47] it has also demonstrated the potential to be used in the production of limonene (limonene is a suitable chemical in the production of industrial diluents, resins and bonding agent and as a dispersing agent for dyes) and BTX (benzene, toluene and xylene).[44,48] Liu *et al.* pyrolyzed waste tyres inside a multilevel reactor under the temperature span of 85–110 °C and 123–145 °C respectively to obtain pyrolytic oil.[49] The authors further refined the oil by employing fractional distillation to achieve significant distillate concentrations of toluene from 7.65% to 68.52% and xylene from 10.09% to 65.20%.[49] It has been stated in the literature that the pyrolysis of waste tyres at lower temperatures of approximately 450 °C yields dipentene; isoprene; other terpenes and aromatics, conversely at higher temperatures above 450 °C their yields are reduced.[50] This occurrence is due to the sustained breaking down or aromatic formation of the monomer compounds. Several authors have obtained high yields of dipentene when pyrolyzing waste tyres, Rofiqul *et al.*[51] obtained yields of 26.42 weight percent (wt%) and 27.75 wt% at temperatures of 425 and 475 °C respectively using truck tyres. Similarly, Arabiourrutia *et al.*[52] obtained a dipentene yield of 23.93 wt% at 425 °C when employing passenger vehicle tyres. It can be deduced that high dipentene yields are obtainable at lower pyrolysis operating temperatures. Recently, significant attention has been given to the benefits of the chemicals obtainable from pyrolysis oil, this is due to the less intensive purification steps associated with the chemical feedstock production as well as the firmly established markets that exist for the chemicals.[48,53] The solid fraction produced during thermochemical conversion is a product of carbon black and other inorganic filling material added in the tyre manufacturing process, and the secondary reactions occurring with the char material during the pyrolysis process.[29] Literature has shown that the optimal operating temperature for char production is 450 °C to 550 °C,[29] a further expansion in temperature results in a reduced char yield. Pyrolytic char contains 85 wt% of carbon (C), has high porosity and, large surface. These properties place carbon black at a favourable advantage for several potential uses, namely; solid fuel in a form of briquettes; as a carbon source (carbon black) in industrial applications; upon further treatment, the activated carbon from tyres can be used as an adsorbent; catalyst aid[54] and as a filler in road pavement.[55] As a carbon black, the solid char is widely applicable in the rubber and tyre manufacturing sector as a filler and colourant in rubber products. Despite the expedient surface morphology of pyrolytic carbon black comprising of comparable properties to industrial carbon black, pyrolytic carbon contains substantial quantities of ash, inorganic impurities and sulphur.[29] Ucar *et al.*,[56] Williams and Brindle,[57] and Gonzalez *et al.*,[58] reported ash quantities of 18.9%, 7.1% and 3.9% respectively as well as sulphur concentrations of 1.71%, 1.7% and 1.5% respectively on passenger car tyres. As activated carbon, solid char is suitable to be used as an industrial adsorbent due to its minimal volume porosity. At present, sawdust; coconut shell and coal *etc.* are the predominantly used sources of industrial carbon black.[59] These natural resources run the risk of depletion in the near future, thus potentially giving rise to a price hike for activated carbon.[29] Affirmatively, waste tyres provide the opportunity to be used as a source for activated carbon production. However, the major drawback is the necessity for further chemical of physical treatment to meet carbon black industrial grade standards. In the agricultural sector, the use of biochar for soil enhancement has gained traction worldwide and has received attention in recent years.[60] Carbon char has been recognized for its capabilities for decreasing soil density, raising soil temperature, refining crop yield and nourishing the soil. But, the major drawback is that the application of carbon char in soil can be harmful to the environment and human health, due to the existence of polycyclic aromatic hydrocarbons and volatile organic compounds, thus limiting its use to some extent. The process economics of pyrolysis have shown that the successes of waste pyrolysis is highly dependant on the quality and applicability of the final product streams. In that regard, Arabiourrutia[61] and Miandad[62] have demonstrated the benefits of waste tyre catalytic pyrolysis while employing natural and synthetic zeolite catalyst as well as acidic and basic catalysts. The advantageous use of catalytic material has been shown to (i) improve the waste tyre pyrolysis gas and liquid yields, (ii) selectively produce valuable chemicals, such as light alkenes or aromatics compounds, (iii) minimize the sulphur content in tyre derived oil and, (iv) increase H_2 content in the gas product.[61]

2. Waste tyres as a thermochemical process feedstock

Commercial vehicle tyres are manufactured from rubber (45–55 wt%), carbon black (20–35 wt%), metal textile (15–25 wt%), zinc oxide (1–3 wt%), sulphur (1–2 wt%) and additives (5–7 wt%).[63] Vehicle tyres consists of a combination of natural (NR) and synthetic rubber (SR), namely; butyl rubber (BR) and styrene butadiene rubber (SBR). NR is employed due to its suitable tear resistant strength, superior bonding strength and rolling resistance. SBR promotes better tyre abrasion resistance and grip properties when compared with NR, also, SBR is widely applied in tyre treads casing and sidewalls.[64] The tyre production pathway includes the vulcanisation process's employment, where a non-reversible reaction among the different chemicals

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Table 2 The proximate and ultimate properties of waste tyres and waste tyre derived oil

Parameters	Proximate and ultimate values of unprocessed waste tyres			Proximate and ultimate analysis of commercial diesel oil	Parameters	Proximate and ultimate values of waste tyre derived oil			
Ref.	80	64	81	73	Ref.	82	83	84	85
Carbon (wt%)	83.45–85.60	83–88	86.64	87.4	Carbon (wt%)	84.2	86.3	82.6	75.50
Hydrogen (wt%)	9.59–11.73	9.6–11.4	10.56	12.1	Hydrogen (wt%)	7.9	7.1	8.2	0.70
Oxygen (wt%)	0.10–3.96	0.1–4.0	0.78	0.29	Oxygen (wt%)	5.5	4.5	6.1	13.10
Nitrogen (wt%)	0.4–1.05	0.4–1.0	1.32	370 (ppm)	Nitrogen (wt%)	1.0	0.5	0.9	0.00
Total sulphur (wt%)	0.72–0.96	0.6–1.6	0.69	0.29	Total sulphur (wt%)	1.4	1.7	2.2	5.60
Calorific value (MJ kg^{-1})	38–42.8	HHV: 41–46, LHV: 31–37	HHV: 42.76	45.5	Calorific Value (MJ kg^{-1})	—	—	—	38.6
Viscosity@40 °C (cSt)	3.2	2–21 (mm^2 s^{-1})	2.60	2.1	Moisture (wt%)	1.8	0.4	1.1	0.80
Flash point (°C)	43	13–60	—	54	Volatiles (wt%)	64.5	59.9	66.8	64.50
Aromatic content (m/m%)	39.3–63	—	—		Fixed carbon (wt%)	26.3	21	28.5	29.60
Density@15 °C (kg m^{-3})	920	900–1000	888.29	838	Ash (wt%)	7.4	18.4	3.6	5.10

and feed materials results in crosslinks of rubber polymeric sequences of strong bridges between molecules. The cross-linked elastomers are rigid, insoluble and inseparable thermoset.[47] Waste tyres possess a relatively high heating value (38–45.0 MJ kg^{-1})[14] relative to other waste materials such as biomass (22.2–28.5 MJ kg^{-1}),[65] food waste (3.667–9.920 MJ kg^{-1}),[66] animal manure (12–15 MJ kg^{-1})[25] and plastics (24–44 MJ kg^{-1})[67] as well as common fossil fuels such coal lignite (16.98 MJ kg^{-1}) and subbituminous (33.04 MJ kg^{-1}).[68]

Waste tyres are a popular thermochemical process feedstock due to their high carbon content, as deduced from Table 2. The carbon content of waste tyres, tyre derived oil (TDO) and conventional diesel oils is comparable. As a result, this makes the solid char produced favourable for use in the carbon black industry. Commercial carbon blacks have been reported to have an elemental carbon content of approximately 97.00 wt%.[69] Zhang *et al.*, after employing the pickling process on pyrolytic char, reported a carbon content increase from 81.79% to 97.18%, thus, making pyrolysis derived char comparable with commercial carbon blacks.[70] TDO is one of the main products of interest when employing thermochemical processes. A comparison study of the properties of waste tyres, TDO and conventional diesel oils is carried out in Table 2. The flashpoint of TDO is essentially lower than that of commercial diesel fuel, this brings about fire concerns pertaining to the suitability of oil storage and transportation. Zhang *et al.*, has attributed the low flash point to the high presence of volatile hydrocarbons in the TDO.[14] The high density of TDO has damaging effects in the combustion engine's performance and also generates sulphur dioxide (SO_2), noxious oxide (NO_x), carbon monoxide (CO), hydrocarbons and smoke emissions in the exhaust gas.[71] Lastly, a low viscosity is preferred for the purpose of aiding oil pumping and engine performance. Comparing the properties of TDO with those of conventional diesel oil, it can be said that the two oils can be paralleled together. However, the upgrading of TDO with chemical and physical techniques may be explored to further enhance the properties of TDO. Physical properties such as distillation; have been found to enhance TDO general properties of crude TPO, namely: density, viscosity, heating value and flash point.[72] Desulfurization, hydrotreating has been found to reduce sulphur and water content,[73] hydro-denitrification removes nitrogen compounds,[14] also, other chemical treatment processes may be employed.

TDO has been shown to have the potential to be used in different industries, a few of the industries are discussed in the section to follow. Several authors have performed the practise of TDO blending with diesel with the aim of enhancing the fuel properties of TDO and to better the emission performance.[14] Umeki *et al.*[74] observed that the mixture of TDO and diesel reduced the density and dynamic viscosity, whereas the heating value displayed a directly proportional increase with increasing diesel content. Lastly, Karagoz *et al.*[75] noted that the cetane number of the blended oil mixture was reduced to quantities lower than conventional diesel standard, as a result, this considerably affects the combustion properties and gas emissions. As a result, more work still needs to be done due to the substandard performance of the TDO and diesel blend pertaining engine and combustion performance as well as the produced higher emission levels. Limonene is reported to be a high-value primary material in the chemicals industry with several noteworthy applications. It can be utilized as a natural cleaning solvent, in the production of fragrance, adhesives, pigment dispersant agents and as a food-additive.[50] The presence of benzene, toluene and xylene (BTX) in TDO had given the waste product renewed attention due to their wide industrial use. Benzene is used to synthesize pigments, rubber, fibres, plastics *etc.*; toluene is used in the industry to produce medicines, pesticides, dyes and xylene is mainly utilized in the production of plastics.[14]

3. Gasification technology

Gasification is a sub-stoichiometric thermochemical process that transforms carbon-based feedstock through gasifying agent's controlled supply into a fuel gas.[76,77] The chemo-physical observations that transpire during the gasification of tyres are

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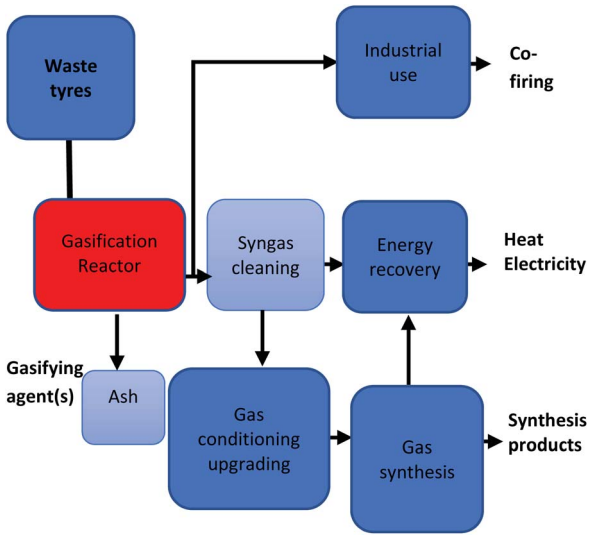

Fig. 1 Waste tyre gasification process pathway.[36]

generally similar to conventional carbonaceous material subjected to thermal depolymerization. This comprises of drying, devolatilization, heat conduction, fissuring, shrinkage, and fragmentation of solid particles.[78] The gasification process is more multifaceted than the pyrolysis process, it consists of heterogeneous and homogeneous reaction mechanisms. During the heterogeneous reaction, the chemical reactions occurs over the surface of the material, as a result, the rates of conversion is highly depend on factors such as surface area, surface ease of access, carbon active sites, concentration of inorganic matter, and the composition of the gasification agent.[54] In contrast to the heterogeneous reactions, the homogeneous reaction are nearly instantaneous under elevated thermal conditions.[79] The initial depolymerization reaction entails the decomposition of tyres resulting in heavy and light hydrocarbons as well as solid char.

The secondary reactions include the disintegrating of the heavy hydrocarbons, the reforming of light and heavy hydrocarbons and the further volarization of the solid char fraction to expand gas production.[86] The resultant synthesis gas (syngas), encompasses a complex mixture of H_2, CO, carbon dioxide (CO_2), methane (CH_4) and other light hydrocarbons. Fig. 1 illustrates a basic waste tyre gasification process pathway and reactions R1 to R10 shows the reactions involved in the gasification process.[87] Lee *et al.*[88] proposed that the application of R1 to R10 reaction during the steam reforming of municipal solid waste rubber can also be applicable for the gasification of waste tyre. Reactive agents such as air, oxygen (O_2), steam/water, H_2 (ref. 36) and CO_2 (ref. 89) can be utilized as gasifying agents.

Heterogeneous reactions

Char partial combustion

$$C(s) + 0.5O_2(g) = CO(g)\ (-111\ MJ)\ (kmol)^{-1} \quad (1)$$

Boudouard reaction

$$C(s) + CO_2(g) \leftrightarrow 2CO(g)\ (+172\ MJ)\ (kmol)^{-1} \quad (2)$$

Water–gas reaction

$$C(s) + H_2O(g) \leftrightarrow CO(g) + H_2(g)\ (+131\ MJ)\ (kmol)^{-1} \quad (3)$$

Methanation

$$C(s) + 2H_2(g) \leftrightarrow CH_4(g)\ (75\ MJ)/(kmol) \quad (4)$$

Homogeneous reactions

CO partial combustion

$$C(s) + 0.5O_2(g) = CO(g)\ (-283\ MJ)\ (kmol)^{-1} \quad (5)$$

H_2 partial combustion

$$H_2(g) + 0.5O_2(g) = H_2O(g)\ (-242\ MJ)\ (kmol)^{-1} \quad (6)$$

CO shift

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g)\ (-14\ MJ)\ (kmol)^{-1} \quad (7)$$

Steam methane reformimg

$$CH_4(g) + H_2O(g) = CO(g) + 3H_2(g)\ (+206\ MJ)\ (kmol)^{-1} \quad (8)$$

Hydrogen sulphide and ammonia formation reactions

H_2S formation

$$H_2(g) + S(s) = H_2S(g) \quad (9)$$

NH_3 formation

$$0.5N_2(g) + 1.5H_2(g) = NH_3(g) \quad (10)$$

Sulphur (S), nitrogen (N), hydrogen sulphide (H_2S), ammonia (NH^3), gas (g), solid (s)

The heating value and the resultant gas constituents are highly reliant on the gasifying agent amongst other factors.[40] Air gasification has been advanced to industrial scale due to its abundant availability.[90] However, some of the advantages of employing air as a gasifying agent are the high nitrogen concentration in the product gas and the reduced lower heating value (LHV), 4–6 MJ N m^{-3}.[91] The inverse can be said regarding the use of oxygen as a gasifying agent, oxygen must be purchased or generated at a cost for use in the process. However, it yields a final product gas of higher LHV (10–15 MJ N m^{-3}) and low nitrogen concentration.[92] In that regard, choosing between air and oxygen as a gasifying agent will be highly dependent on the application of the final product as well as the economical evaluation of the process. Fig. 2 presents all primary and secondary product stream pathways.

Gasification of various feedstocks including waste tyres has shown high potential to produce high-quality syngas, however, typical gasification systems have not been developed efficiently to reduce the substantial amounts of energy required to breakdown the feed material.[90] Also, one of the most critical gaps is the lack of regulatory framework certainty in some emerging countries and the costs associated with the establishment of gasification facilities remain capital intensive, this

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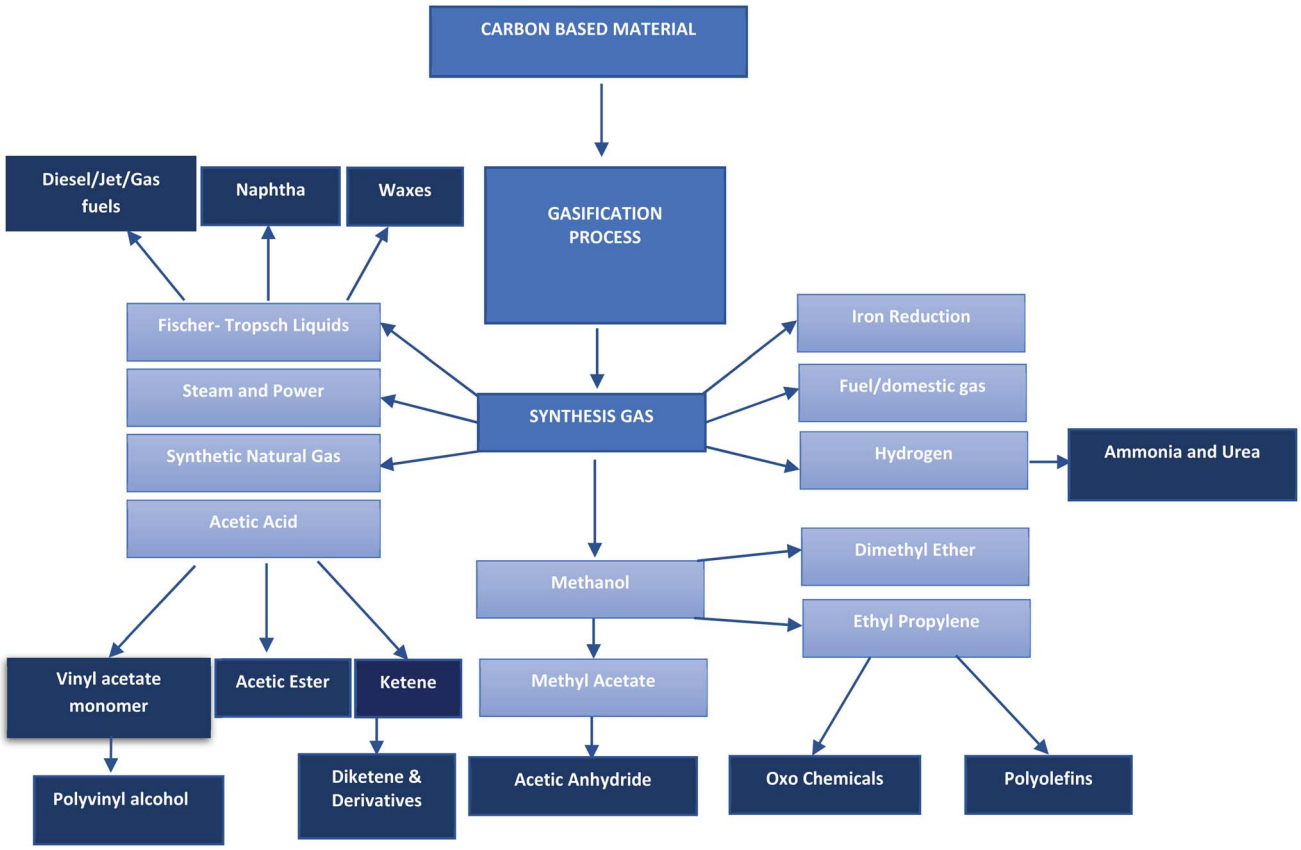

Fig. 2 Gasification process primary and secondary product streams.[123]

is unlikely to change soon. Significant factors such as feed material size, moisture, gasifying agent, equivalent ratio and temperature play a pivotal role in the gasification system and in addition influence product yield.[93]

3.1 The effect of process parameters

3.1.1 The effect of reactor design. Literature studies have been conducted that assess the benefits and shortcomings of the fixed and fluidized bed gasifiers.[93–95]

Alauddin *et al.*[96] observed several weaknesses in the fixed bed gasifiers. The authors determined that the inconsistent heat and mass transfer between the solids in a fixed bed reactor resulted in excess tar formation, while the fluidized bed promoted adequate contact of solids with the gas. Moreover, the use of bed material further enhances the heat transfer between the solids and gas, allowing various feedstock and or varying sizes to be utilized in the fluidized bed reactor.[96]

3.1.2 The effect of temperature. Unsound process temperature control can affect syngas composition, thus, influencing product quality and in the long run its final applications. According to Le Chatelier's principle, elevated temperatures promote the formation of products under endothermic conditions while reactants are favoured under exothermic conditions, such trends in gasification have been observed by.[87,92,96] Waste tyres of 3 mm to 5 mm were steam gasified at a temperature range of 600 °C to 800 °C and produced gas yields from 0.21 m^3 kg^{-1} to 0.76 m^3 kg^{-1}, this is attributed by the temperature's modification of the thermodynamic behaviour of the reactions. However, the heating value was significantly reduced from 9.6 MJ m^{-3} to 22.2 MJ m^{-3}.[85] Furthermore, the authors concluded that using steam in the reactor resulted in improved gas yields when compared to other gasifying agents.[97] This phenomenon can be justified by the fact that when steam is used as a gasification agent, the process tends to yield a product gas containing more H_2 per unit of carbon, resulting in a higher H/C ratio and the formation of hydrocarbons.[92]

3.1.3 The effect of moisture content. Literature surveys have shown that reducing moisture content in the feed material promotes increased energy efficiency and improve syngas quality.[39,92,98] Basu further emphasized that the presence of minimal moisture in the material results in improved heat recoveries in the product gas.[92] Syngas has several domestic and industrial applications, it can be utilized to produce electricity in gas engines or turbines, utilized as a source of heat, used in the manufacturing of fuels and chemicals, and utilized in a catalytic process to produce speciality products.[99,100]

3.1.4 The effect of gasifying agent. Lv *et al.*[101] investigated the effect of air–steam biomass gasification in a fluidised bed reactor. The authors concluded that purging in steam to biomass gasification enhances gas quality, in contrast, excessive steam lowers the gasification temperature and reduces gas quality. Parallel work was conducted by Gonzalez *et al.*[102] to

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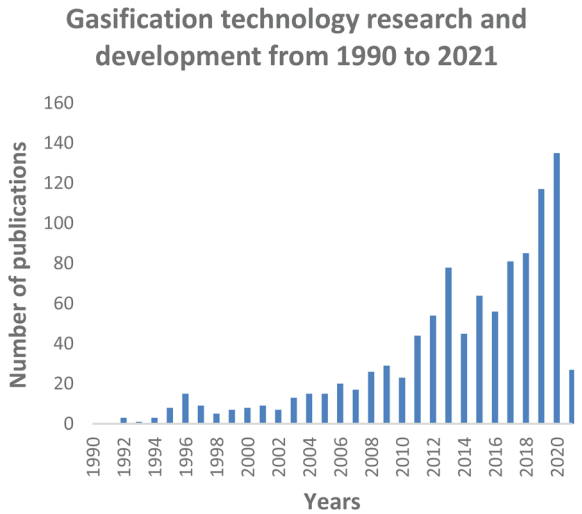

Fig. 3 Gasification technology research and development trends: data extracted from Scopus and science direct search engines, 30 December 2020.

compare the effect of steam and CO_2 when utilized as a gasifying agent. The results showed that activated carbon yielded from steam gasification had greater permeability and surface area as compared to those produced using CO_2. Moreover, Karatas *et al.*[103] gasified waste tyres while employing varying gasification gases such as air and CO_2; air and steam and steam alone in a bubbling fluidized bed gasifier. As a result, the authors observed the heating values of air and CO_2, air and steam and steam to be 9.59, 7.34 and 15.21 MJ N m^{-3} respectively. Lastly, in two distinctive work where the author utilized steam and air as gasifying agents. Karatas[104] realized that steam gasification produced gas with greater H_2 content (55–57%) and LHV (30–37 MJ kg^{-1}), while the inverse can be said about air, a low hydrogen content (15–20%) and LHV (4–7 MJ kg^{-1}) we obtained during air gasification. The results observed above from different authors prove that steam gasification is favourable to the following gas properties (i) quality, (ii) heating values and, (iii) H_2 content. Furthermore, the permeability and surface area of activated carbons produced from steam gasification were significantly improved.

3.1.5 The effect of particle size. Lee and Kim[105] gasified waste tyres in a laboratory sized thermo-balance reactor using air as a gasifying agent with a varying particle size range of 0.025 to 0.1 cm. The authors concluded that tyre gasification rate was not dependent on particle size. On the contrary, pulverized tyres were gasified in a laboratory-scale fluidized bed gasifier air at a temperature ranging from 350 °C to 900 °C.[106] The authors determined that the equivalence ratio, tyre feed rate and particle size affect the gasification final product composition and yield, the bed temperature, and the heating value.

3.2 Research and developments in gasification

Research and development trends show that a substantial amount of research studies have been directed towards the advancement of the gasification system. In 1801, the water–gas shift reaction was explored by Fourcroy,[11] subsequently, in 1861 the first gasifier unit, the Siemens gasifier, was installed and operated successfully.[107] This led to the first commercial gasifier that operated predominantly for solid fuels and later advancements to process various fuels were explored. In the latter years, the gasifier played a critical part in the development of industrial power and heat applications up till the end of the 1920s.[95] World War II also contributed immensely to the mass manufacturing of compact gasifiers between 1920 to 1940.[4] During this period, syngas was utilized to power commercial vehicles, used for domestic lighting and cooking, applied in agricultural and industrial machines and other various sectors.[92,95] However, towards the end of the war, the discovery of copious amounts of fossil fuel in the Middle East became evident, thus, ending the reliance and the era of compact gasifiers. Nevertheless, research into improving the gasification systems continued resulting in the ground-breaking establishment of a continuous gasification system by Carl Linde in 1920. The fluidized bed and pressurized moving bed gasifiers were developed in 1926 and 1931 respectively.[107] The energy crisis experienced during the 1970s ignited renewed interests in the gasification processes. The technology yet again offered an alternative and reliable source of energy especially for growing industries in emerging countries that could not keep up with the burden of increased costs of petroleum in the world market whilst possessing rich resources of biomass. Developing countries like the Philippines, Brazil, Indonesia, and India also introduced gasifier application programs based on locally developed technologies.[95]

The Scopus and Science Direct databases were used to collect all the literature that was ultimately used for comparison of the thermochemical processes. From a research point of view, an assessment into the growth, development and trends of the gasification system during the past three decades is shown in

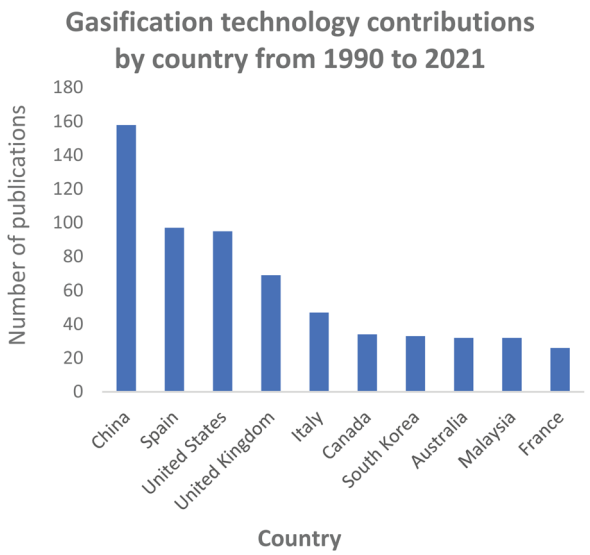

Fig. 4 Gasification process research and development contributions by country: data extracted from Scopus and science direct search engines, 30 December 2020.

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Fig. 3. Amid this period, researchers were starting to critically look at the benefits such as energy, heat and chemical recovery potentials that the gasification process can offer to the growing energy demand, fossil fuel depletion crisis as well as the adverse climate change effects caused by fossil fuels. The various fixed bed reactors (downdraft, updraft, and cross draft); fluidized bed reactors (bubbling bed and circulating bed) and continuous gasification reactors are now well researched, understood and documented in literature.[95]

In Fig. 3, a generally growing interest in gasification research is evident. The increase is immensely contributed by (i) the mass availability of various feedstock material, including waste materials; (ii) the well-defined operating parameters; (iii) the well-understood types of gasification reactors; (iv) the vast domestic, commercial and industrial final application capabilities, and (v) the use of catalysts to develop the process and/or the final generated products. During the 2014–2016 period, inconclusive research attention is noticeable for the gasification field. However, this phenomenon is followed by a sharp increase in research interest due to the Chinese Government's investment in Clean Coal Technology Programs as part of its National Energy Plan.[108] This is further demonstrated by Fig. 4 which highlights the large contribution and investment that China has made towards gasification. Records show that China has the highest number of gasification facilities that are mostly being operated at industrial and commercial scale.[108] The year 2020 sparked the largest interest in gasification compared to the past three decades, with research records showing about 135 publications on the gasification process. To date in the year 2021, 27 gasification publications have already been produced thus, presenting a mounting interest in gasification research and advancements. This can be perceived as a significant step that has contributed towards the alleviation of the high dependency on conventional fossil fuels.

In Fig. 4, the top 10 countries that have made significant progress in gasification technology are shown. China, Spain and the USA have contributed significantly into the continuous advancement of the gasification process utilizing a diversity of feedstocks, for instance; waste tyres and waste rubbers, assorted municipal waste, biomass and coal. Countries such as India, China, and most of Southeast Asia share a common trait of high fossil fuel prices due to little or zero fossil fuel reserves. However, they have large reserves of low-grade coal creating a robust market for coal-derived natural gas facilities. On the contrary, coal gasification for power generation has been regressing in the USA, with many of the planned projects being abandoned.[109] In North America, the materialization of plentiful and affordable natural gas has resulted in coal gasification to be less attractive and viable. Coal is the primary resource of energy in China, contributing 65% to the country's energy need.[45] China has employed a vast range of gasification technologies, even extending its use domestically. An assortment of coals is gasified to produce various products including ammonia, oxo-chemicals, methanol, prolyplene, acetic acid, butanol, octanol, urea, ethylene glycol, syngas, dimethyl ether, and liquified petroleum gas.[45] Researchers such as Williams, Olazar and Bilboa, shown in Fig. 5, have actively contributed to

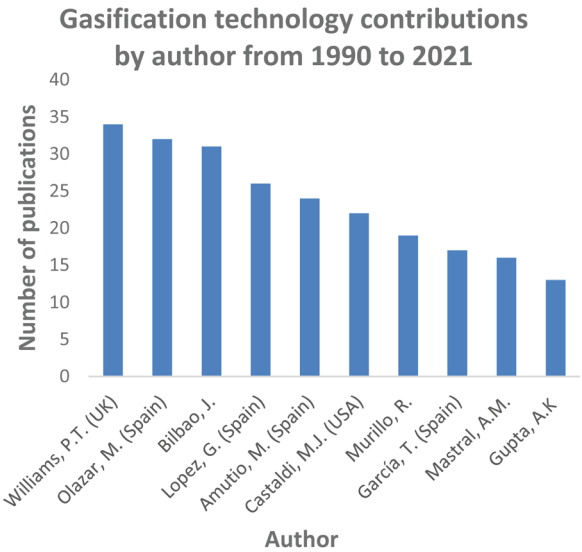

Fig. 5 Gasification technology research and development contributions by authors data extracted from Scopus and science direct search engines, 30 December 2020.

the development of the gasification technology through their published studies and subsequent applications. Williams has fundamentally concentrated on the effect of Nickel (Ni) catalyst on pyrolysis-gasification for hydrogen production and tar removal from biomass feedstock.[110–112] The author also extended his research and collaborations with other researchers to investigate gasification parameters' influence on final products using feedstocks such as waste tyres and plastics.[113,114] Lastly, Williams[115] together with Elbaba[116,117] and Wu,[114,118] pioneered the hydrogen production process through the gasification of waste tyres and plastic waste products. Olazar, Balboa and Lopez collaborated on the further studies and development of the conical spouted bed reactor[119–121] contributing comprehensively to the understanding of the effect and advantages of mechanical modifications on the conical spouted bed reactor. Moreover, their partnership further expanded on the steam gasification of biomass, plastics and their co-gasification subsequently.

3.3 Case study: gasification facilities

Numerous prominent gasification facilities that produce a wide range of products from various feedstocks are operational throughout the world. The top 20 gasification plants ranked according to their energy output are presented in Table 3, these plants are of commercial-scale with reported viable technology. Coal remains the predominant feedstock to date, with 65% of the plants utilizing various coal types. The pearl gas to liquid (GTL), located in Qatar, is the largest facility in term of energy output and employs the most recent cutting-edge technology. South Africa currently has numerous gasification plants in operation, these facilities are discussed in the sections to follow. Sasol Synfuel II in South Africa is the longest standing chemical plant and contributes to about 28% to South Africa's total petroleum demand[122] and R21 billion or 2% to the national

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Table 3 Worldwide commercial gasification plants[126]

Gasification plant name	Location	Gasification technology	MIWth[a] SG output	Startup year	Feed	Product
(1) Pearl GTL[b]	Qatar	Shell	10 936	2011	Natural gas	TFL[h]
(2) Sasol synfuels II (west)	South Africa	Lurgi FBDB[e]	7048	1977	Subbituminous coal	TFL[h]
(3) Sasol synfuels III (east)	South Africa	Lurgi FBDB[e]	7048	1982	Subbituminous coal	TFL[h]
(4) Inner Mongolia chemical plant	China	Shell	3373	2011	Lignite coal	Methanol
(5) Shenhua Ningxia coal-to-polypropylene	China	Siemens	1912	2011	Coal	Methanol
(6) Great plains synfuels plant	USA	Lurgi FBDB	1900.3	1984	Lignite coal	SNG
(7) Shenhua Ningxia coal-to-olefins plant	China	GE[f]	1750	2011	Coal	Methanol
(8) Hexignen SNG[c] plant	China	SEDIN	1670	2012	Coal	SNG
(9) SURLUX IGCC[d] project	Italy	GE[f]	1300	2000	Visbreaker residue	Electricity
(10) ISAB energy IGCC project	Italy	GE[f]	1203	1999	Rose asphalt	Electricity
(11) Sanwei Neimeggu methanol plant	China	GE[f]	1167	2011	Coal	Methanol
(12) Edwardsport IGCC[d]	USA	GE[f]	1150	2013	Coal	Electricity
(13) Tianjin chemical plant	China	Shell	1124	2010	Coal	
(14) Henan Jinkai	China	HT-L	1120	2012	Coal	Ammonia
(15) Yunnan methanol & DME plant	China	BGL[g]	1120	2011	Coal	Methanol
(16) Bintulu GTL[b] plant	Malaysia	Shell	1032.4	1993	Natural gas	FT liquids
(17) Long lake integrated upgrading project	Canada	Shell	1025	2008	Asphalt	Hydrogen
(18) Leuna methanol plant	Germany	Shell	984.3	1985	Visbreaker residue	Hydrogen
(19) Amuay Flexicoker	Venezuela	Flexi-coking	966	1980	Petcoke	Flexi-gas
(20) Shenhua erdos	China	Shell	861	2008	Coal	Hydrogen

[a] Megawatt thermal (MWth). [b] Gas-to-liquid (GTL). [c] Synthetic natural gas (SNG). [d] Integrated gasification combined cycle (IGCC). [e] Fixed bed dry bottom (FBDB). [f] General electric (GE). [g] British gas lurgi (BGL). [h] Transportation liduid fuels (TLF).

Table 4 Prominent gasification plant in South Africa

Gasification plant name	Facility owner	Location	Gasification technology	No of units	Output (MWth)	Startup year	Feed	Product
(1) Mossel bay GTL refinery	PetroSA	Mossel bay, W.C	Lurgi comb. Reforming	3	3040	1992	Natural gas	Liquid fuels
(2) Sasol ammonia plant	Sasol	Sasolburg, Free state	Uhde reforming	1	241	1993	Natural gas	Chemicals
(3) Theunissen UCG[a] plant	Independent power producer	Theunissen, Free state	UCG[a]	6	142	2020	Coal	Power
(4) Majuba UCG[a]	ESKOM	Volksrust, Mpumalanga	UCG[a]	1	125	2018	Coal	Power
(5) Durban refinery hydrogen plant	Engen petroleum pvt. Ltd	Durban, Kwazulu Natal	Reforming	1	63	2016	Syngas	Hydrogen

[a] Underground coal gasification (UCG).

gross domestic product (GDP).[1] Other gasification facilities currently exist in South Africa, they are of lesser sizes and capacity as compared to Sasol Synfuel West and East, however, these facilities play a significant role in the South African economy. The facilities and their detailed process information are presented in Table 4.

According to Kerester,[123] approximately 25% of the world's ammonia and 30% of the world's methanol is manufactured *via* the gasification process. The Sasol ammonia plant employs the Haber–Bosch process in the coal gasification stage of the oil to produce its ammonia.[122] In the latter process, ammonia stripped from the gas liquor is of very high purity which is used in a variety of industrial applications throughout South Africa. The operation produces 30 200.00 megaton per annum of ammonia. The Theunissen UCG plant employs the mining technology that unearths previously abandoned coal reserves through a gasification process that converts the coal into syngas. Records show that two-thirds of the earth's coal reserves are not economically

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mineable through conventional mining techniques,[124] UCG offers a workable alternative to extract these deep coal reserves economically. The Theunissen UCG facility is planned for operation in the second quarter of the year 2020.[124] The operation is planned to produce 54 MW of electricity. Eskom presently generates 88% of its electricity from coal.[125] This indicates a high dependency on coal for power generation due to its excessive abundance in South Africa. However, Eskom identified the need to employ ecologically friendly technology and the need to fully utilize previously inaccessible coal reserves. This gave birth to the Majuba UCG facility, the 5000 N m^3 h^{-1} pilot plant saw its initiation in January 2007, however, the facility has been in full operation since 2018 and currently produces 100 MW of electricity.[126] The Durban refinery hydrogen plant is operated by Engen Petroleum Ltd and generates 17 000.00 N m^3 h^{-1} of hydrogen from syngas by employing reforming technology.[126]

4. Pyrolysis technology

Pyrolysis is an endothermic chemical degradation process of organic compounds under an oxygen-deprived environment. The inert environment is achieved by purging inert gases such as N_2, Argon or flue gas. The inert gas serves the following purposes; it protects the organic material from oxidation, it meticulously blends the reaction environment, brings equilibrium to the temperature and concentration distribution, assists in discharging volatile pyrolysis products, and it is also a transporter of thermal energy.[127] The pyrolysis process has been known to follow complex pathways that several chemical reactions can not distinctively defined. However, Li *et al.*[128] classified the reactions involved in tyre pyrolysis into three groups, namely; (i) primary pyrolysis reaction that occur at temperature ranges of 250 °C to 520 °C where the pyrolysis thermal decomposition process transpires in accordance to a radical chain reaction whereby dehydrogenation advances along with the decomposition of the chief polymer chain; (ii) secondary subsequent-cracking reaction of volatiles occurring at 550 °C to 800 °C which promote the development of aromatic and polycyclic aromatic compounds that are attributed to a Diels–Alder cyclization reaction (depicted in Fig. 6), predominantly at elevated temperatures and/or long residence times, and (iii) the pyrolytic carbon black gasifying reaction in the presence of $CO_2/H_2O/O_2$ gases at temperature ranges of 750 °C to 1000 °C.[47] The gaseous segment is mainly composed of the following compounds: H_2, CO, CO_2, CH_4, C_2–C_5 paraffin compounds, C_3–C_5 olefin compounds and minute concentrations of sulphur (H_2S, SO_2), carbonyl sulphide (COS), carbon disulphide (CS_2), and nitrogen (NH_3) containing compounds. Natural or synthetic rubber decomposition produces C_4–C_5 hydrocarbons, while secondary cracking reactions are responsible for forming lighter compounds. Arabiourrutia *et al.* determined that the employment of catalysts endorse the occurrence of secondary cracking reactions at elevated temperatures, as a result, this yielded more light hydrocarbons compounds from the further decomposition of larger molecules.[61] The liquid fraction of waste tyre pyrolysis produces

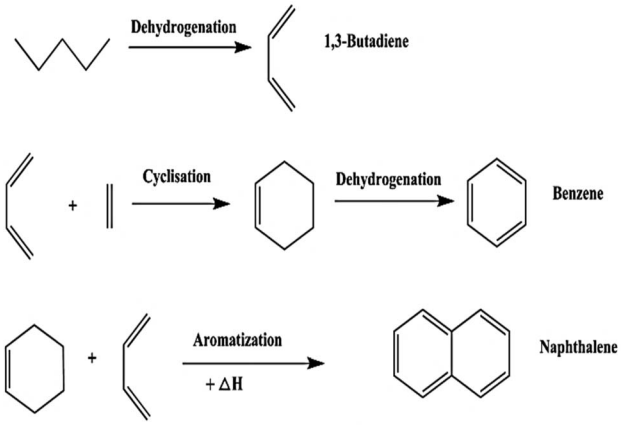

Fig. 6 The Diels–Alder cyclization reaction for the production of polycyclic aromatic hydrocarbons from waste tyres.

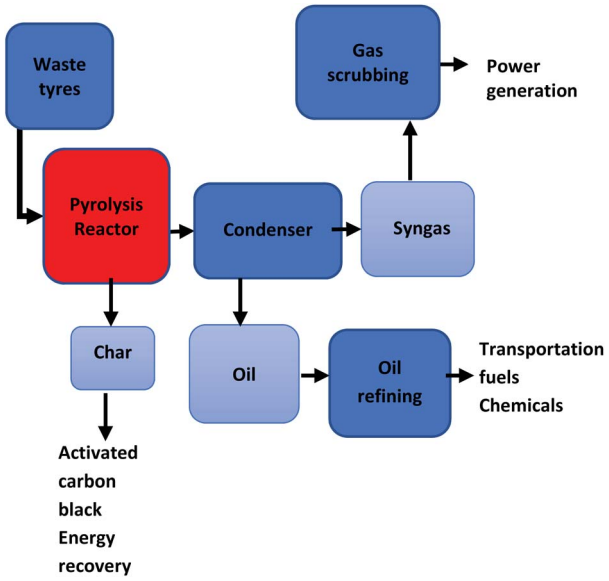

Fig. 7 Waste tyre pyrolysis process pathway.

a mixture of paraffins, olefins and aromatic compounds with a high heating value in the order of 40–45 MJ kg^{-1}.[50] Various types of pyrolysis processes have been comprehensively researched over the years and their process conditions are now well defined and understood.[39] In Fig. 7, a typical pyrolysis process pathway is depicted and reaction 11 (ref. 92) shows the basic pyrolysis reaction. The typical operating temperature employed in pyrolysis ranges between 500 °C to 800 °C with gas, liquid, and char being the three primary products.[39] The composition and percentage yield of each product is highly reliant on the operating conditions, the feed material and the category of the pyrolysis process preferred.[129]

The generation of combustible gas from carbon-based materials is an ancient technique. Egyptians used liquids generated through the pyrolysis process such as tar and pyroligneous acid to preserve their mummies, similarly, the Macedonians attained wood tar from the combustion of biomass in

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pits.[130] By the end of the 18th century, methodologies to reclaim and apply condensable pyrolysis products were fairly well established. As a result, brick kilns were employed instead of conventional pits which generally did not capture the gases.[131] In the 19th century, the wood distillation industry capitalized on the by-products generated from charcoal and liquid fuel production to manufacture chemicals such as methanol, acetic acid, and acetone.[130]

$$C_nH_mO_p + \text{heat} \Rightarrow \sum_{\text{liquid}} C_aH_bO_c + \sum_{\text{gas}} C_xH_yO_z + \sum_{\text{solid}} C \qquad (11)$$

The 20th century saw a rise in the petrochemical industry resulting in the deterioration of the pyrolysis industry. However, the oil crisis brought about renewed attention by shifting focus to alternative technologies.[130] In the early 1980s, the fast pyrolysis process was comprehensively studied resulting in its commercialization,[131] during this time, the focused was on identifying the rigorous operating conditions that can maximize product yield. The 1990s saw new and innovative pyrolysis oils upgrading strategies and the beginning of research into alternative products to replace petroleum. The exponential growth in oil prices accompanied by the impact of global warming due to conventional and outdated technologies has created a demand for pyrolysis fuel and char production. The mid-2000s saw the growth in pyrolysis products' possible applications with the latest trend being the application of pyrolytic char for soil enhancement.[132] The potential use of pyrolysis oil directly in internal combustion engines has been explored by several researchers,[133–135] However, its use currently presents several drawbacks such as the high sulphur content, the existence of benzothiazole and alkylated dibenzothiophenes and the presence of dense molecules constituting to high boiling points.[136]

4.1 The effect of process parameters on the pyrolysis process

4.1.1 The effect of tyre composition on product yield. The composition of a tyre is influenced by the manufacturing brand, age and tyre category[137,138] which as a result affects the final pyrolysis product distribution and physiochemical characteristics. Kyari *et al.*[138] pyrolyzed seven different passenger car tyre brands in a fixed bed reactor under the same process conditions. The authors reported distinctions in the gas constituents for the various tyre brands and the gross calorific values for the gas varied between 29.9 MJ m^{-3} and 42.1 MJ m^{-3}. Also, distinctions in the aromatic composition were observed in the liquid product yields. The conflicting results are attributed to the different blends of raw material that are employed during tyre production. The most common tyre categories are; passenger car tyres, motorcycle tyres and truck tyres, these different tyres exhibit different compositions of natural rubber (NR) and synthetic rubber (SR), the commonly used synthetical rubbers are butyl rubber (BR) and styrene–butadiene rubber (SBR). Truck tyres have been reported to contain twice the quantity of NR and a ratio of 4 : 3 for SR when paralleled with passenger car tyres.[47] In literature, Ucar, *et al.*[56] determined that truck tyres with a NR content of 51 wt% produced 15.4 vol% aromatic content, whereas, passenger car tyres with a lesser NR content of 35 wt% yielded a higher aromatic content of 41.5 vol%. Consequently, passenger car tyres are inclined to chemical production due to their greater aromatic concentration, meanwhile, truck tyres are likely to be suitable in the production of automobile fuel due to their lower sulphur concentration.[139]

4.1.2 The effect of temperature on product yield. One of the main variables that affect the pyrolysis process and product distribution is temperature.[47] Laresgoiti, M. F. *et al.*[140] reported an optimum operating pyrolysis process temperature of 500 °C. At lower temperatures, key compounds such as SBR, BR and NR remain in the pyrolytic carbon char. Conversely, an increase in temperature enhances the production of the gas fraction but compromises the oil yield. Islam[141] pyrolyzed motorcycle tyres of 4 cm^3 particle size in a fluidized bed reactor at 425 °C. The authors reported gas, liquid and char yields of 9.0 wt%, 47.0 wt% and 44.0% wt% respectively. Similarly, Kar[142] obtained gas, oil and char yields of 50.7, 46.2 and 3.0 wt% respectively when 10 g of waste tyres were processes in a fixed bed reactor at 375 °C. At the recommended optimum waste tyre pyrolysis of 500 °C, Lopez[143] performed the pyrolysis of less than 0.1 cm waste tyre particle size in a conical spouted bed reactor, the author reported 57.0 wt% oil yield, 4.5 wt% gas yield and 35 wt% solid char yield. Likewise, Roy *et al.*[144] reported significant oil yield of 62.2 wt% when tyre particle sizes of 0.125 cm were employed in a vacuum pyrolysis reactor at 500 °C. At higher temperatures of 700 °C, Lucchesi and Maschio[145] pyrolyzed waste tyres in a continuous counter-current fluidized bed reactor under a nitrogen and CO_2 environment and obtained gas yields of 26.7 wt%, oil yield of 36.6 wt% and char yields of 36.7 wt%. Moreover, Zang *et al.*[146] processed waste tyres of 0.025–0.085 cm particle size in a vacuum pyrolysis reactor at 600 °C, the authors reported gas yield of 16.8 wt%, liquid yield of 48.8 wt% and char yields of 34.8 wt%. From the above literature, it is evident that a direction proportional relationship exists between the gas yield and temperature, also, longer residence times cause the occurrence of secondary reactions in the reactor hot zone that further volatilize the liquid to gas, ultimately resulting in reduced oil yields.

4.1.3 The effect of heating rate on product yield and reactors. In addition to temperature, the heating rate strongly affects pyrolysis process product yields. The heating rate can be used to categorize the pyrolysis process as either slow; fast or flash, and influences the retention time of material in the reaction chamber.[147] The employed heating rate is also associated with the reactor type, and specific reactor types produce higher heating rates.[148] Continuous reactors such as auger reactor (AR), bubbling fluidized bed reactor (BFBR), circulating fluidized bed reactor (CFBR), conical spouted fluidized bed (CSBR), rotary kiln reactor (RKR) are commonly associated with constant temperature values and the temperature gradient remains fixed along the process. The heating rates in these reactors is very high and are strongly influenced by the reactor attributes.[47] The above observations suggest that low heating

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rates favour the production of solids, while elevated heating rates promote gas production.

4.1.4 The effect of pressure on product yield. Numerous authors have investigated the effect of pressure on pyrolysis product yield and product properties. Buekens reported an increase in oil viscosity with increasing atmospheric pressure.[149] Conversely, Roy *et al.*[150] and Martinez *et al.* [47] determined that pyrolysis under vacuum pressure increased oil yields by reducing the occurrence of secondary reactions. Moreover, the reduction in secondary reactions limited gas accumulation around the char external area, making the char more valued as a carbon adsorbent with increased pore capacity. Lopez *et al.*[143] reported similar findings, the authors determined that the positive pressure gradient generated by vacuum resulted in the quicker dispersion of the volatiles into the particle, thus, lowering their retention time and reducing the occurrence of secondary reactions.

4.1.5 The effect of particle size on product yield. P. Parthasarathy *et al.*[147] determined that reduced feed material particle sizes promote efficient conversion and decrease the material and energy needs for the system. On the other hand, larger particle sizes increase carbon black yield, but, compromise oil yield. Osayi *et al.*[151] processed waste tyres at a temperature of 600 °C; heating rate of 15 °C min^{-1} and various particle sizes of 0.2 cm, 0.4 cm, 0.6 cm, 0.8 cm, and 1 cm. The author reported pyrolytic liquid yield increases from 24.5 wt% to 34.4 wt% for 0.2–0.6 cm particle size; however, a further increase in the particle size to above 0.6 cm resulted in a decline in oil yield. Generally, a gradual increase in char yield and a decrease in gas yield was noticed within an increase in particle sizes of 0.2–1 cm. Likewise, Islam *et al.*[141] observed a similar trend when motorcycle tyres were processed in a fixed bed reactor at 475 °C and particle volume sizes of 2, 4, 6, 8, 10 and 12 cm^3. An upsurge in pyrolytic oil yield was observed up to 49 wt% for the feed size of 4 cm^3, subsequently, a gradual reduction in oil yield was noted for larger particle sizes with the lowest yield recorded at 45 wt% for 12 cm^3 particle size. Moreover, the gas yield was observed to decreased while char yield increased with increasing particle size. The increases in oil yields are attributed to the reduced particle feed size which affords more reaction surface of the material resulting in rapid decomposition. The increase in char yield results from the larger material not being entirely decomposed and remaining carbonized in solid form.

4.1.6 The effect of retention time on product yield. Extended retention times have been reported to promote secondary reactions and alter the final product distribution and properties.[47] Olazar *et al.*[152] established that elevated temperatures require rapid tyre retention times and reduced temperatures require extended retention times. Experimental results showing an alike trend were presented by Islam *et al.*,[141] the authors processed 4 cm^3 motorcycle tyres at 475 °C in a fixed bed reactor at varying retention times of 5, 10, 15 and 20 seconds. Under an increasing vapour retention time of 5–20 seconds, the oil and char yields were reduced while the gas yield increased due to the further volarization of liquid product to secondary permanent gases.

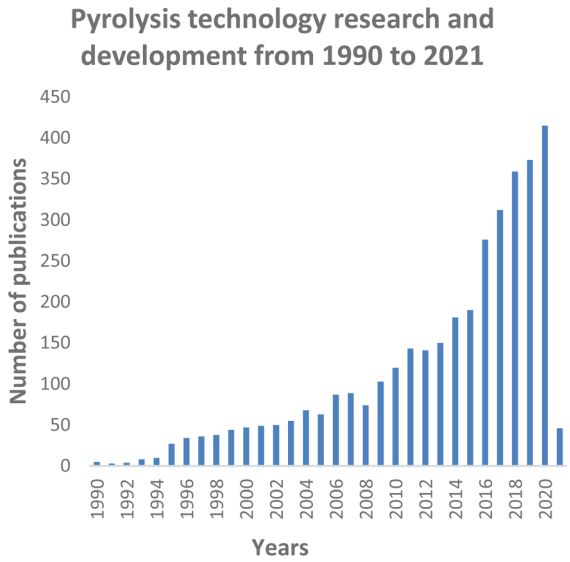

Fig. 8 Pyrolysis technology research and development and trends: data extracted from Scopus and science direct search engines, 30 December 2020.

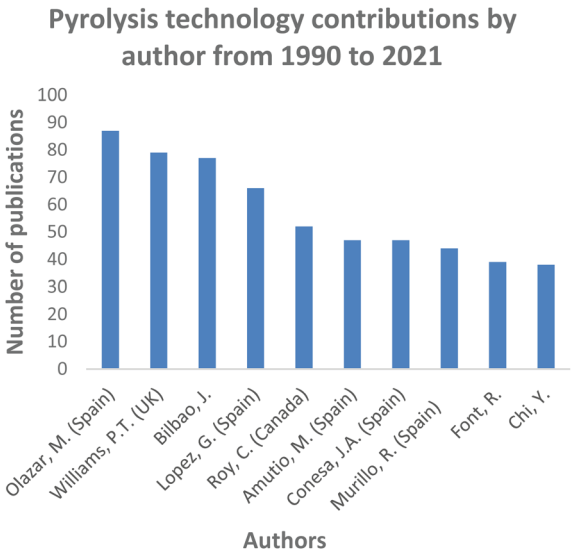

Fig. 9 Pyrolysis technology research and development contributions by authors: data extracted from Scopus and science direct search engines, 30 December 2020.

4.2 Research and developments of the pyrolysis process

Pyrolysis technology is constantly evolving with significant research and development still ongoing. The technical expertise on how the technology works is well defined. However, the commercialization of the process is still in its infancy stages. An evaluation of the progress made over the past thirty years of research is mapped out in Fig. 8. Essentially, it can be said that a great deal of research has been channelled towards the pyrolysis technology since the early 1990s. When comparing the trend for all three technologies, namely pyrolysis; gasification and liquefaction. The pyrolysis trend shows a continuously

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growing trend with a few declines in research interest experienced during the years 2005 and 2008. The year 2020 sparked the highest figure in pyrolysis research through the production of 415 research outputs, this depicts a constant increasing research interest in the process as well as the advancements to improve the technology. Several authors have made significant contributions towards the development and well documentation of pyrolysis literature through the research work they have embarked on, shown in Fig. 9. Olazar, Bilboa and Lopez have comprehensively researched various aspects of pyrolysis such as catalytic pyrolysis[153–155] the co-pyrolysis conversion of plastics, waste tyres and biomass,[121,156,157] reactor design advancements, concentrating on the conical spouted bed reactors[158–160] and the application of pyrolysis products.[161] The authors have also collaborated with Mkhize, Danon and Van Der Gryp[162] to expand research of waste tyre pyrolysis and the conical spouted bed reactor's improved design. Willian P. T. has immensely contributed towards hydrogen production through the pyrolysis of solid waste,[117,118,163] biomass gasification,[164] carbon nanotubes,[165,166] waste tyre pyrolysis,[86–89] and the advancement of thermochemical technologies.[63,167,168] The author also contributed towards co-pyrolysis using various waste materials[169–171] and the development of different pyrolysis processes.[57,172,173] Roy C. contributed significantly towards the pyrolysis of non-conventional materials such as animal meat and bone,[174] tar sands,[175] bituminous roofing waste materials,[176] sugarcane bagasse with petroleum residue,[177] PVC plastics,[178–180] and electrical cables[181] to produce various products. Also, Roy C. has focused on applying carbon blacks and their comparison with commercial-grade carbon blacks[182,183]

Similarly, with the gasification technology, China has invested immensely into the pyrolysis process as illustrated in Fig. 9. China has been classified as one of the world's rapidly growing economies leading to large-scale urbanization and high waste generating rates. China generated 188.51 million tons of municipal solid waste in 2016, with 99% being produced in 214 major cities.[184] The total quantities have been estimated to reach 323 million tons and 480 million tons by 2020 and 2030 respectively.[185] The number of waste processing facilities in China have increased from 74 in 2008 to 286 in 2017 with plans to increase the capacity by 54% by 2020.[186] The waste to energy industry has grown momentously in China with the Chinese government fully endorsing such initiatives and has developed standards to support this industry. During the 1995 to 2000 period, Spain reported the highest MSW generation rates in the EU of 520 and 660 kg per capita,[187] composting from 43 to 72 per capita and waste to energy initiatives increased from 70 to 120 per capita.[188] Regardless of the high MSW generation statistics recorded during this period, landfilling rates declined from 300 to 160 kg per capita, while upsurges in recycling rose from 50 to 132 kg per capita, composting from 43 to 72 per capita and waste to energy initiatives increased from 70 to 120 per capita[188] Spain currently operates 10 waste to energy facilities which have played a critical role in the reduction of waste quantities being diverted for landfilling.[187]

Table 5 Prominent pyrolysis plants in the world

Gasification plant name	Location	Units	Start-up year	Capacity	Product	Ref.
(1)	US, Canada, europe, Brazil, Malaysia				Biofuels and chemicals	
(1.1) Red arrow, WI	Canada	Circulating fluidised bed		1700 kg h^{-1}	Chemicals	203 and 204
(1.2) Red arrow, WI		Circulating fluidised bed	1996	1500 kg h^{-1}	Chemicals	203 and 204
(1.3) Ensyn engineering	University of West Antario	Ultra-pyrolysis: circulating fluidised bed		30 kg h^{-1}	Oil	203 and 204
	Finland	Fast pyrolysis in a circulating fluidised bed	2013	20 kg h^{-1}	Oil 65–75 wt%	203–205
(2) DynaMotive	Canada	Bubbling fluidized bed	2001	400 kg h^{-1}	Oil 50–75 wt%, char, gas	203 and 204
(3) Bio-alternative	USA			2000 kg h^{-1}	Char	203 and 206
(4) Battelle	Ohio, USA	Catalytic pyrolysis technology	2013	1000 kg h^{-1}	Transportation fuels	207
(5) Empyro	Hengelo, Netherlands	Flash pyrolysis	2015	5000 kg h^{-1}	Oil, chemicals, electricity	208 and 209
(6) Cool planet energy system	Louisiana, US		2016	10 kg h^{-1}	Biofuels (fuel and carbon black)	210
(7) Anellotech	Texas, USA	Catalytic pyrolysis, fluidized bed reactor	2008	500 ton/day	Chemicals (BTX) and fuels	211
(8) Bioliq	Germany	Fast pyrolysis	2005	500 kg h^{-1}	Chemical and fuels	212
(9) Proton power	Tennessee, USA	Fast pyrolysis	2009		Biochar, fuel and electricity	213 and 214

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Table 6 Various pyrolysis facilities in South Africa

Gasification plant name	Location	Start-up year	Feed	Product	Ref.
(1) IRR manufacturing	Pretoria, Gauteng	2013	1000 kg h^{-1}	Pyrolytic gas, oil and char	194
(2) Recor	Gauteng South			Pyrolytic gas, oil and char	195
(3) TRIDENT fuels pty ltd	Germiston, Gauteng			Crumb rubber, pyrolytic char	215
(4) Osho SA recycling (pty) ltd	Pretoria, Gauteng		40 ton per day	Oil, char and steel wire	216
(5) Enviroprotek (pty) ltd	Nigel, Gauteng	2018	500 ton per month	Pyrolytic oil, char and steel wire	196
(6) PPC (de Hoek)	Cape town, Western cape	2016	8000 ton per year	Tyre derived fuel	191 and 192
(7) Mathe group	Hammasdale, KZN	2012	30–40 ton per day	Crumb rubber	193 and 217
(8) Dawhi rubber recycling	Germiston, Gauteng		16 ton per day	Crumb rubber	195
(9) Earth tread pty ltd	Edenvale. Gauteng	2011		Rubber products: paving, roof tiles	196
(10) Langkloof bricks	Jeffrey's bay, EC	1999	25 000–40 000 per month	Tyre derived fuel: cement kiln	190
(11) Tyre energy extraction pty ltd	Coega, EC	2012	42 ton per day	Carbon black	218

4.3 Case study: pyrolysis facilities

Several well-established pyrolysis facilities exist in different sections of the world, the most prominent are located in Canada, the USA, Finland and other countries. Countries like Finland use the vastly available biomass and hydropower to provide heat to households throughout the cold winter months.[189] Table 5 outlines some commercial and prominent pyrolysis plants that are currently operational worldwide. Biomass is the favoured feedstock of choice due to its abundance and consideration as waste. South Africa has also had numerous successes and failures when it comes to operating pyrolysis facilities currently operating waste tyre pyrolysis or processing plants that produce a variety of end products for various applications are shown in Table 6.

The country currently has numerous successful waste tyre processing facilities. These plants range from modest waste to energy utilization of waste tyres, where facilities such as Langkloof Brickworks and PPC (De Hoek), utilize waste tyres concurrently with coal for their cement manufacturing process. This initiative has substantially reduced energy consumption, minimized CO_2 emissions by 50%,[190] reduced the usage of coal by 15% and lowered nitrous oxide emissions.[191] Other cement manufacturing companies such as AfriSam, La Farge and Natal Portland Cement have implemented the same approach and are realizing the benefits of co-processing coal with waste tyres in their manufacturing process.[192] Waste tyres exhibit a high heating value than coal and can be a reliable source of fuel for technologies such as combustion, incineration *etc.*, and for industrial applications such as in cement kilns, boilers and smelters.[37] This technology is fairly modern is South Africa, however, countries such as the USA, Germany and Japan have been employing this technology since the 1970s.[28] Ambient mechanical grinding processes where whole tyres are fragmented to crumb rubber is another common technique used to reclaim waste tyres. In this technology, mechanical equipment including shredders, rolling mills and granulators disintegrate the tyre at ambient temperature while the steel wires are removed electromagnetically.[73] Facilities such as Trident Fuels pvt. Ltd, the Mathe Group and Dawhi Rubber Recycling employ this technology. Passenger vehicle and truck tyres are grounded to yield diverse grades of crumb rubber and powders for various applications, such as hard flooring, groundworks for sports

Table 7 The advantages and disadvantages of the different waste tyre processing technologies employed in South Africa

	Energy recovery	Mechanical grinding	Pyrolysis
Advantages	Non-complex system	Numerous successful markets exist crumb rubber	Higher calorific value products
	System normally has no moving mechanical parts	Minimal waste generated	Energetically self-sufficient
	Size minimization not required		Accommodates the employment of catalyst to ensure maximum yield of products and a stable reaction process
	Less environmentally hazardous		Processes a large variety of feed material
Disadvantages	May require gas cleaning system	Extra energy required for mechanical moving parts and cooling	Higher plant capital costs
	Ash disposal is a limitation		

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grounds and, for the road construction sector. The Mathe Group has reached commercial success in the crumbing of waste tyres in over 20 African countries which include Namibia, Zambia, Botswana, Congo *etc.*[193] Lastly, several commercial entities, such as IRR Manufacturing, have employed the pyrolysis of waste tyres at a large-scale capacity of approximately 24 tonne per day while employing a continuous pyrolysis kiln.[194] The pyrolysis company processes end-of-life tyres, waste wood, and waste polyolefin plastics to generate pyrolytic oil, gas and high-grade carbon char for the global market. Pyrolysis oil produced at 500 litres per hour is utilized in the marine industry. The carbon char produced at 30–380 kg per hour is briquetted and used as a solid fuel, however, further treatment of the char produces recovered carbon black (rCB) that is by ASTM International Standards approved and applied for use in rubber, plastics, and pigment industries.[194] Recor-Renewable Energy Corporation, treats a vast diversity of wastes such as metropolitan solid; agricultural; health; abattoir and wood dust to convert them to energy. Moreover, waste tyres are pyrolyzed to produce energy, pyrolytic oil and char, while plastic and waste oils are treated to produce a range of diesel grades.[195] Lastly, Enviroprotek (pvt.) Ltd, is a small scale waste tyre processing plant that processes 16 000 kg per day of waste tyres in a batch vacuum pyrolysis reactor to produce oil, char and steel wires.[196] These pyrolysis plants have shown some level of success with the longest running being in operation since 2013, this proves that waste tyre pyrolysis together with the right process economics and profitable product markets can be a viable business. Table 7 compares the advantages and disadvantages of the different waste tyre processing technologies currently employed in South Africa.

5. Liquefaction technology

Direct liquefaction involves the breaking down of carbon-based material at elevated temperature and pressure to form a crude liquid product that can be further distilled to form liquid fuels. There are several different methods of production, but the basic process entails the dissolving of carbonaceous material in water or solvent at fairly low temperatures (250–350 °C) and high pressure (5–20 MPa) then subsequently hydrocracking (adding hydrogen over a catalyst).[197] Liquid yields of 70% can be achieved with thermal efficiencies of approximately 60–70%.[197] A schematic pathway of direct coal liquefaction process is shown in Fig. 11. Conversely, indirect liquefaction entails the complete decomposition of carbon-based structures by gasification in the presence of a gasifying agent to form syngas, further treating of the syngas employing the Fischer–Tropsch Process produces liquid hydrocarbon.[198] A schematic pathway of indirect coal liquefaction processis shown in Fig. 12. Danon *et al.*[50] observed that the liquefaction process in rubbers is attributed to the initiation of radical reaction, also, the authors highlighted that the dual bonds in the central polymer are decomposed by the monomer radicals (also known as allylic radicals) developed by β-scission reactions. These radicals are extremely volatile and experience alkylation formation and cyclization to yield various alkenes and alkyls functional groups. At elevated thermal

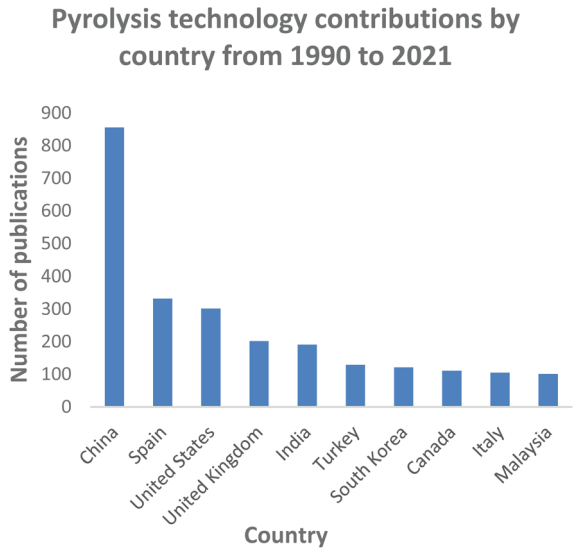

Fig. 10 Pyrolysis technology research and development contributions by country: data extracted from Scopus and science direct search engines, 30 December 2020.

conditions, the disintegration and dehydrogenation reaction mechanism of cyclic compounds from aliphatic compounds results in the development of aromatic hydrocarbons, furthermore, during the hydrolysis reaction, other functional groups such as alcohols, ketones and aldehydes are formed.[199]

Coal is a common substrate for liquefaction in countries deprived of a firm distribution of petroleum such as Germany (during World War II) and South Africa (since the early 1970s).[200] According to Lumpkin,[201] direct liquefaction was established by I. G. Bergius in Germany in the 1930s, the

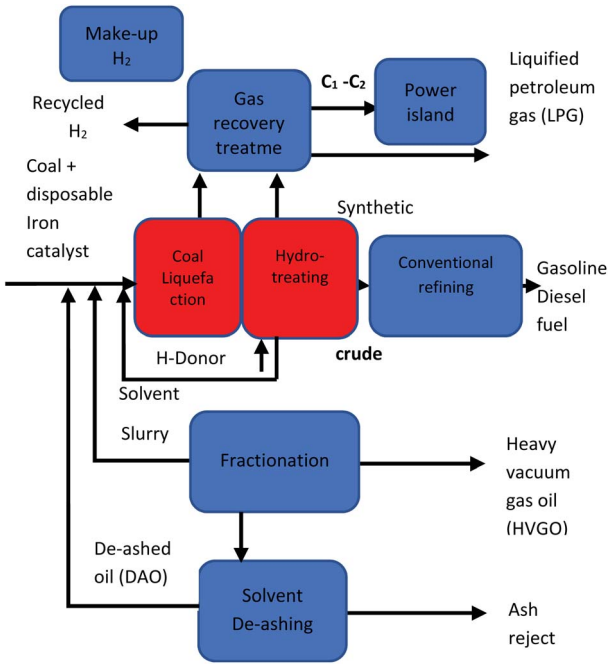

Fig. 11 A schematic pathway of direct coal liquefaction process.[241]

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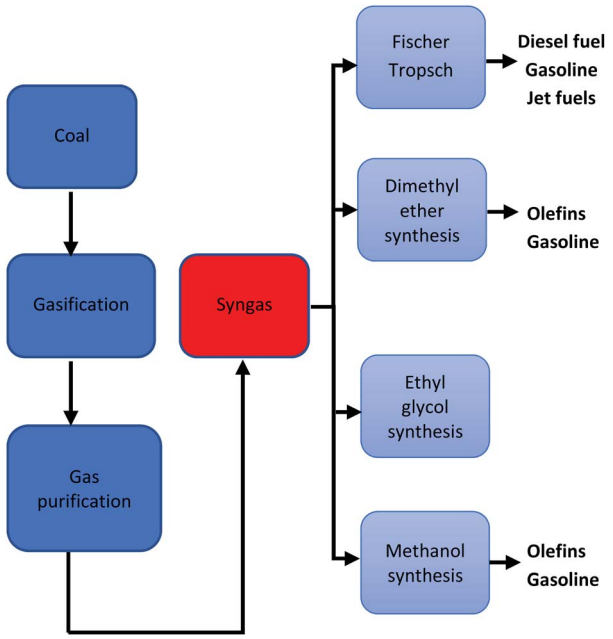

Fig. 12 A schematic pathway of indirect coal liquefaction process.[249]

research included the reacting of coal with H_2 at elevated pressures and temperatures. The Bergius process was commercially applied in 1927 by Farben in Germany during the Second World War and supplementary plants were instituted in the 1930s in the former Soviet Union and Czechoslovakia.[202] Furthermore, small scale plants were operated in Japan and Great Britain. These plants ceased operation due to their economical non-viability. Direct liquefaction research and development progressed after the war and increased considerably amid the oil crunch in the 1970s.[202]

5.1 The effect of process parameters

5.1.1 The effect of raw material and temperature on product yield. Liquefaction product yield is affected by various parameters such as feed material category, temperature, pressure, reaction time, heating rate, solvent type, and catalyst.[39] Huang *et al.*[219] investigated three different feedstocks' liquefaction, namely rice straw, sewage sludge and algae (*Spirulina* spp.) under the same reaction conditions. The results showed that higher conversion rates are obtainable with Spirulina liquefaction.[219] However, sewage sludge yielded the greatest bio-oil yield. The bio-oil hydrocarbon (C_{17} and C_{20}) distribution for sewage sludge and Spirulina were comparable, whereas C_8 hydrocarbons were prominent in rice straw.[219] Moreover, liquefaction of dry municipal refuse, dried sewage, and straw were studied at the University of Manchester Institute of Science and Technology. The findings showed that oil yields of about 35 wt% were obtainable in the temperature range of 250–400 °C and 10 MPa pressure.[220]

Brand *et al.*[221] researched the impact of reaction temperature on biomass conversion, bio-oil yields, solid fraction, and gas composition. The authors determined that raising the temperature from 280 °C to 400 °C resulted in a considerable increase in bio-oil yield from 15.8 wt% to 59.9 wt%, gas yield increased from 18.2% to 36.0%, and a significant decline in solid residue from 66.0 wt% to 1.9 wt%.[171] The gas composition was altered with reaction temperature in the following standard ascending trend $CO > CO_2 > C_2H_4 > CH_4 > C_2H_6$.[222] The CO_2 and CO gas production can be attributed to the disintegration of oxygen-based compounds found in the biomass while CH_4 is generated from methoxyl groups. Likewise, Jena *et al.*[223] and Chan *et al.*[224] obtained similar findings and reaction trends for similar experiments. Williams *et al.*[134] investigated tyre pyrolysis in a fixed bed reactor at 300 °C to 720 °C with heating rates from 1 °C min^{-1} to 80 °C min^{-1} and concluded that liquid production was raised with rising heating rates. Likewise, Gonzalez *et al.*[225] employed a fixed bed reactor at heating rates ranges of 5 °C min^{-1} to 20 °C min^{-1} and a temperature of 600 °C. A final liquid yield of 55.4% was obtained at a heating rate of 15 °C min^{-1}. This is a consequence of the intensified cracking of at greater heating rates. Quek and Balasubramanian[48] observed that reduced pressures, raised temperatures and heating rates produced higher oil yields.

5.1.2 The effect of pressure and reaction time on product yield. Brand *et al.*[221] investigated the influence of inert N_2 pressure on biomass product yield. The authors concluded that the N_2 pressure had an insignificant influence on the conversion and the yields of bio-oil, gas and solid liquefaction final products. Conversely, Behrendt *et al.*[226] applied Le Chatelier's principle and established that bio-oil yields ascended with increasing pressure. Furthermore, Brand *et al.*[221] studied the influence of reaction time on conversion rates and bio-oil yield. The authors increased the reaction time from (t–t_o) to 60 min and found that the conversion rate increased from 65.9% to 89.6% and bio-oil yield was altered from 37.1 wt% to 52.0 wt%. Also, additional increases in reaction times to 240 min improved conversion and oil yield to excesses of 93.6 wt% and 59.2 wt% respectively.[221] Thus, it can be deduced that the interactions between temperature, pressure and heating rate are the most paramount operating factors in the liquefaction process.

5.1.3 The effect of solvent on product yield. The University of Sherbrooke (Quebec, Canada) studies the effect of solvent type on the liquefaction process. Aspen wood and cellulose were treated in aqueous, non-aqueous, creosote, and ethylene glycol media.[227] Liquid yields of 40–60% were obtained at 340 °C in a tubular reactor system.[228] In addition to water, organics such as methanol, ethanol, acetone *etc.*, have been employed as reaction solvents.[36] According to Chumpoo *et al.*,[228] ethanol has proven to be the most efficient solvent for biomass liquefaction when taking into account efficiency, environmental friendliness and reproducible ability.[228,229]

5.1.4 The effect of catalyst on product yield. Catalysts have proven in many thermochemical processes to be one of the most crucial variables that influence the reactions, hence, optimum catalyst selection is paramount.[39] Researchers have comprehensively researched various catalysts in the liquefaction process, these have included alkali-based catalysts (carbonates and hydroxide forms of Na, K)[230,231] Nickel (Ni) in sulphate form,[232] catalysts on silicon oxide (SiO_2)/aluminium oxide (Al_2O_3) support,[233] sulfides of iron (Fe)[233] and metal

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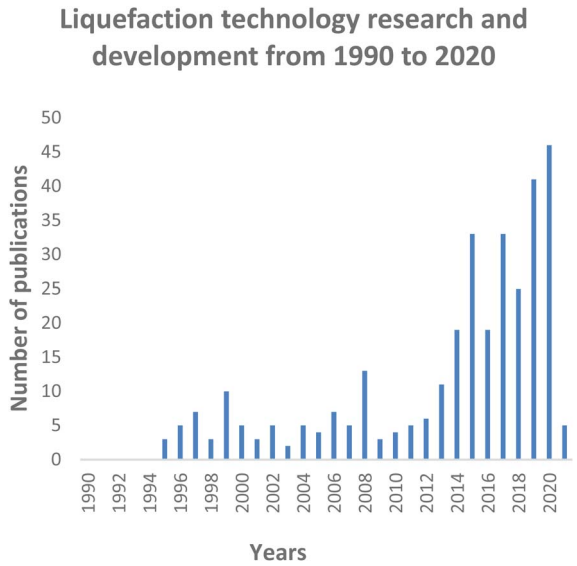

Fig. 13 Liquefaction technology research and development trends: data extracted from Scopus and science direct search engines, 30 December 2020.

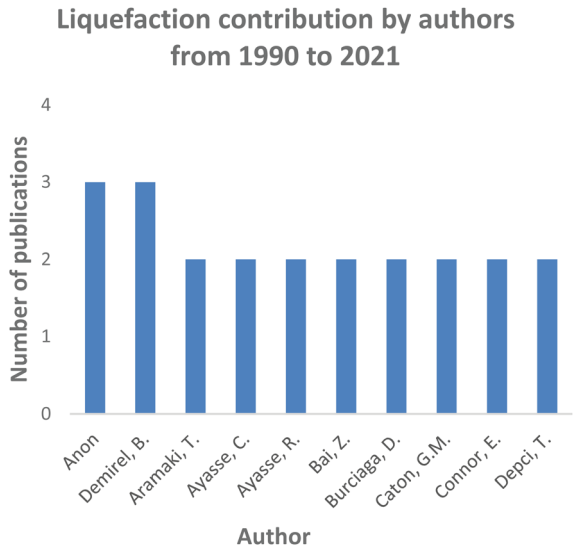

Fig. 14 Gasification process research and development contributions by authors: data extracted from Scopus and science direct search engines, 30 December 2020.

catalysts such as rhodium (Ru), molybdenum (Mo) and platinum (Pt).[234,235] In liquefaction technology, catalysts are known to fundamentally reduce the activation energy, increase liquid yields and improve conversion efficiency by approximately 10–50% depending on the catalyst in use.[236]

Liquefaction offers numerous benefits over other thermochemical processes. The overall process efficiency is typically higher in liquefaction, the employed process temperature and pressure are lower when paralleled to the gasification process and the produced liquid fuels possess a higher energy density as compared to gas fuels.[237] Fig. 10 and 11 shows the direct and indirect coal liquefaction process pathway respectively.

5.2 Research and developments in the liquefaction process

Direct liquefaction research died down in the mid to late 1980s[202] up until the technology was re-established during the mid-90s as shown in Fig. 13. The 2017 global coal to liquid fuels market was estimated at 3.88 billion USD,[238] regardless of the decline experienced in 2016 as shown in Fig. 13. In the year 2010, China invested in cleaner coal technologies for fuel supply, thus significantly contributing to the liquefaction technology advancement. The overall liquefaction trend in Fig. 13 shows significant inconclusive results with the development of the technology. However, the liquefaction technology market is expected to expand in the years to come as shown on the growing trend from 2018 to the present. This trend is strongly influenced by the declining dependency on natural gas and crude oil's natural reserves to produce transportation fuels as per the current industry status quo. Several authors have contributed immensely in the research and development of liquefaction technology, as shown in Fig. 14 Anon (1982),[239] (1989)[240] played a significant role.

Since the 1980s in the development and application of coal technology in various thermochemical processes, as well as the co-processing of various coals for the production of oils. Mochida reviewed the liquification technology comprehensively in the early 2000s[242,243] Demirel (2007)[244–246] further developed the Rentech coal to liquid fuel technology to commercialization. Lastly, Ayasse and Ayasse (2015),[247] (2016)[248] investigated the Fischer–Tropsch process pairing with new gas to liquid technology. The authors reported that pairing these technologies together increased the gas to diesel fuel conversion ratio.

China is the leading country in the global coal to liquid research and development with the highest quantity of actively

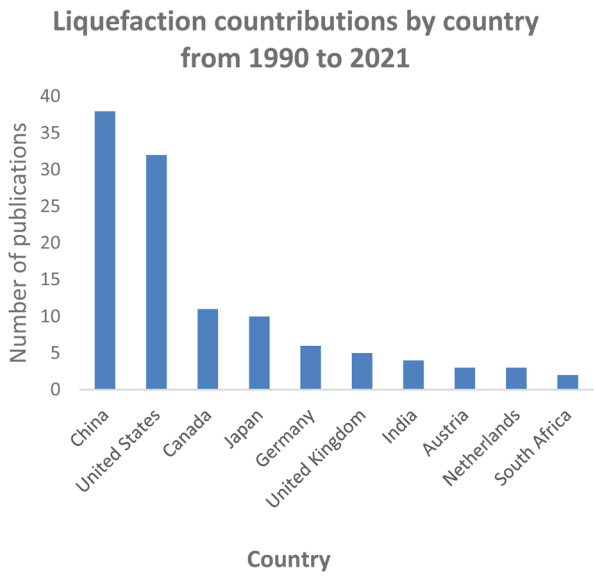

Fig. 15 Gasification process research and development contributions by countries: data extracted from Scopus and science direct search engines, 30 December 2020.

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Table 8 Waste tyre gasification, pyrolysis and liquefaction technology comparison

Process	Gasification	Pyrolysis	liquefaction
Process definition	Gasification is a sub-stoichiometric thermochemical process that transforms carbon-based feedstock through the controlled supply of a gasifying agent into a fuel gas	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	Liquefaction is the thermochemical conversion of an organic solid into a petroleum-like liquid
Process conditions			
Reaction environment	Reducing (oxidant amount lower than that required by stoichiometric combustion)	Total absence of any oxidant	Direct liquefaction may involve the use of solvents such as water and indirect liquefaction employs the use of a gasifying agent
Reactant gas	Air, pure oxygen, oxygen-enriched air, steam	None	Solvents and gasifying agents occasionally employed
Temperature	550–1000 °C	500 and 800 °C	250–350 °C
Pressure	Atmospheric	Slightly above atmospheric pressure	5–20 MPa
Process outputs			
Gas product	CO, H_2, CO_2, H_2O, CH_4	CO, H_2, CH_4, paraffins, olefins	CO, H_2, CH_4, paraffins, olefins
Liquid product	Gasification generates small amounts of oil due to thermal cracking and steam reforming reactions at elevated temperatures, however, a condensable fraction of tar and soot is generated	Pyrolysis produces oil that has properties identical to diesel and can be employed as fuel. It contains a high aromatic content, thus can function as an industrial chemical feedstock	Liquefaction produces a liquid product comprising of viscous molecular compounds with properties comparable, but not alike, to those of petroleum-based fuels
Solid product	Bottom ash is often the residual product that can be directly utilized as backfilling material for road construction. Upon further upgrading, the char has the potential for activated carbon production	The pyrolysis char has a high carbon content and can utilized fuel. Upon further treatment, the char can be utilized for the manufacturing of carbon black, activated carbon and in similar industries	
Pollutant	H_2S, HCl, COS, NH_3, HCN, tar, alkali, particulate matter	H_2S, HCl, NH_3, HCN, tar, particulate matter	SO_x, NO_x, CO

operating facilities, eight plants on record[238] and the largest number of publications as shown in Fig. 15. In 2017, China unveiled several indirect and direct coal gasification and liquefaction projects. The Chinese government is keenly investing in manufacturing synthetic fuels from coal to reduce its reliance on imported petroleum.[238] South Africa, India and Indonesia are some of the developing countries that have made advancements in the liquefaction technology. South Africa developed the coal-to-liquid technology in the 1950s during an oil deficiency period, the technology currently plays an integral part in the South African economy.[131] The technology is considered economically viable in countries which have vast coal resources.[132]

The overall waste tyre gasification, pyrolysis and liquefaction technology comparison is depicted in Table 8.

6. Conclusion

From literature, it is evident that thermochemical conversion processes have over the previous decades played an essential role in the;

- diverting of certain waste streams from landfill sites,
- production of value-added final products that can be a source of fuel, energy and chemicals and,
- in the creation of green jobs from the establishment and operation of thermochemical PGL facilities.

In addition, abundant literature has been developed to define the operating factors such as temperature, pressure, particle size, heating rate, the use of solvent, types of reaction environment, reactor configuration and the use of catalysts which ultimately influence product yield and quality. The authors established that general agreements can be found with some of these factors but no overall relationship can be deduced.

The following highlights were realized from the study:

- There has been growing world interest in pyrolysis and gasification technologies since the early 1990s to the present times, however, interest in liquefaction technology only commenced during the mid-1990s. Moreover, the trends of PGL research and development show a generally increasing percentage interest in the technologies from 1990 to 2021.
- Many authors have identified a vast range of waste feedstocks, such as; waste tyres, biomass, plastics, food waste, microalgae and animal manure for use in PGL processes. The final products obtained from these waste materials have yielded promising application benefits that can be employed in PGL conversion processes.

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• China has invested immensely into waste to energy initiatives and has demonstrated the vast applications for waste derived products. The country's high population rates has contributed to the generation of large quantities of waste material, which is greatly used in PGL conversion technologies. Furthermore, the country has capitalized in its high abundance of low grade coal which is used in PGL processes.

• PGL technologies employing waste tyres as a feedstock have demonstrated the potential of producing high-end values products in their crude form or refined form, that can be applied in industries such as the energy sector, chemical industry, petroleum industry, rubber manufacturing, solid carbon based industries, pigments and dyes industries, agricultural sector *etc.* However, shortcomings such as (i) the capital intensive costs associated with the establishment of PGL facilities; (ii) the lack of well established and regulated markets for PGL end-products; and (iii) the necessity for further treatment steps for the purpose of enhancing PGL end-products to commercial products alike still exist.

Some of the most critical gaps that were ascertained during this study are:

• Generally, African countries seem to show less interest in the investing into waste to energy initiatives. However, South Africa is steadily showing a keen interest in the development of PGL technologies and has developed various end-product streams for the attained products. Moreover, the country is encouraging the use of waste material as feedstock during these processes.

• The lack of regulatory framework certainty in some emerging countries has proven to be a hinderance in the further development of PGL processes.

Conflicts of interest

There are no conflicts to declare.

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