Energy Potential of Plastic Waste Valorisation: A Short Comparative Assessment of Pyrolysis vs. Gasification

Ana Antelava[a], Natalia Jablonska[a], Achilleas Constantinou[a,b,c]*, George Manos[b], Shakirudeen A. Salaudeen[d], Animesh Dutta[d], Sultan Majed Al-Salem[e]*

[a]Division of Chemical & Petroleum Engineering, School of Engineering, London South Bank University, London SE1 0AA, UK.

[b]Department of Chemical Engineering, University College London (UCL), London WCIE 7JE, UK.

[c]Department of Chemical Engineering Cyprus University of Technology, 57 Corner of Athinon and Anexartisias, 3036 Limassol, Cyprus.

[d]Mechanical Engineering Program, School of Engineering, University of Guelph, Guelph, Ontario N1G 2W1, Canada

[e]Environment & Life Sciences Research Centre, Kuwait Institute for Scientific Research (KISR), P.O. Box 24885, Safat 13109; Kuwait.

*Author to whom correspondence should be addressed to: constaa8@lsbu.ac.uk & ssalem@kisr.edu.kw.

Keywords: Plastic waste, thermochemical conversion, energy recovery, energy integration, fuel.

Graphical Abstract:
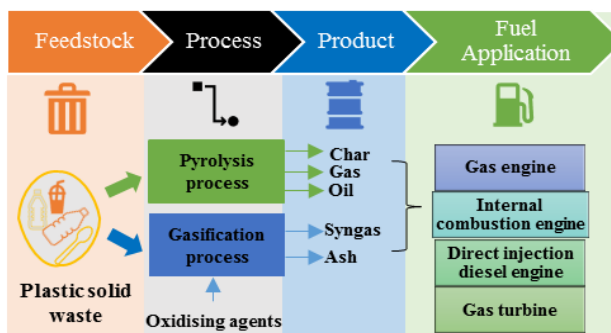
Abstract

Plastics are abundant and have a high energy content making their use in energy applications attractive. This article presents a review on plastic waste (PW) management by pyrolysis and gasification, which are two routes of thermochemical conversion (TCC) techniques. The conversion of PW and the application of its converted products are important steps towards reducing reliance on fossil fuel, enhancing closed-loop recycling of materials and circular economy. The review presented herein also focuses on product distribution and yields with emphasis on the energy content and potential integration to energy systems and grids. It is found that pyro-oils have properties similar to conventional fuels such as diesel and can partially substitute fossil fuels. In fact, the energy content of PW pyro-oils obtained by various researchers range from 41.10 - 46.16 MJ kg^{-1}, which are close to the heating values of conventional fuels, thus are potential candidates for fuel applications. Typical treatment post conversion is also conducted to maintain the quality of the oil produced and the removal of sulphur content to conform with market standards. On the other hand, syngas produced during gasification possesses a lesser potential for fuel applications as its energy content may reach values as low as 20 MJ kg^{-1} in

comparison to pyro-oil. However, depending on the process conditions, it is possible to increase the energy content to values of over 40 MJ kg^{-1}. Additionally, syngas is the building block for many valuable chemicals. With appropriate treatment, the syngas obtained from the gasification of PW can be used in gas engines and can be converted to commercial products such as liquid fuels via the Fischer-Tropsch synthesis. This review also highlights some available commercial-scale plants for the TCC of PW and real-life application of their obtained products. It is noted that the integration of the processes to energy systems is technically and economically feasible. Real-life applications of products obtained from the pyrolysis and gasification of PW in different parts of the world are also discussed. The produced fuels have been used in cooking stoves, burned in a gas turbine, internal combustion engine, and direct injection diesel engine.

1. Introductory remark

Plastics possess numerous benefits to society. However, as the global population grows, the generation of plastic waste (PW) grows with it in a proportional manner. Only in 2015, there has been over 400 million metric tons of various plastics produced globally[1]. **Figure 1** presents the comparison between primary waste production and generation in 2015 by type of plastic. Different types of plastic have different properties. **Table 1** below presents a comparison of physical properties of a selection of plastic types.
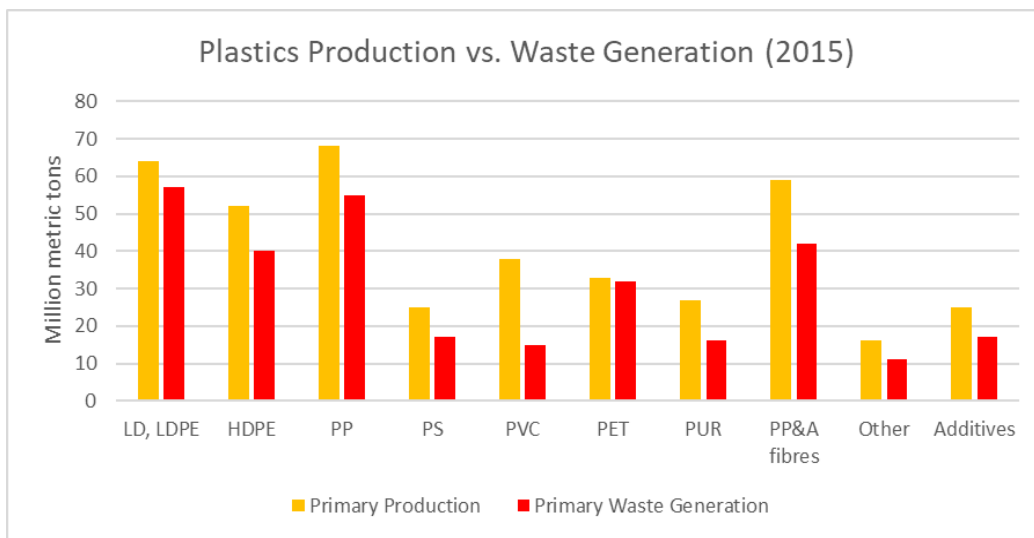
Figure 1. Plastic Production vs. Waste Generation by type of plastic. Based on data from Geyer et al.[1].

Table 1. Physical properties of different types of plastics[2].

Plastic	Low density polyethylene (LDPE)	High density polyethylene (HDPE)	Polypropylene (PP)	Polyethylene Terephathalate (PET)	Polyvinyl chloride (PVC)
Density (kg m^{-3})	919.98	959.98	909.98	1379.96	1419.96
Tensile strength (psi)	1,400	4,000	5,400	11,500	7,500

Plastic	Low density polyethylene (LDPE)	High density polyethylene (HDPE)	Polypropylene (PP)	Polyethylene Terephathalate (PET)	Polyvinyl chloride (PVC)
Flexural Modulus of Elasticity (psi)	30,000	200,000	225,000	400,000	481,000
Water absorption (%)	0.10	0.10	slight	0.10	0.06

Generally, plastic materials are non-degradable and are of single use derived from petrochemical sources such as naphtha, ethylene glycol, styrene, ethylene and propylene[3]. In fact, 50% of plastic commodities are converted and designed with the aim of single-use[4]. This results in a dependence on crude oil production. PW consists of different hydrocarbons (HC) possessing large amount of chemical energy which can be recovered to meet energy demand. Currently, the demand for fuel is growing at an annual rate of 0.7% due to the increase of the global population[5]. It is projected that the recycling of all PW across the global could provide the same energy as 3.5 billion barrels of oil per year[6]. Within a European context, 27.1 million tonnes of PW were collected back in 2017, of which 27.3%, 31.1% and 41.6% was landfilled, recycled and recovered energetically[7]. In a worldly view, PW is on an increasing trend as well in clear proportionality with the global population. The world population has sharply increased between 1950 (2.5 billion) and 2017 (7.6 billion)[8]. Majority of the world population now are living in urban environments relying on plastics commodities on a daily basis. 4.2 billion of the global population are characterised as *'urban population'* as of 2019[9]. Furthermore, recent estimates show that 4.9 billion tonnes of PW were discarded between 1950 and 2015[10]. Sustainable waste management remains a major challenge nowadays. The concept of circular economy (CE) is a very appealing way to reduce the accumulation of PW in a sustainable manner by applying the 4R concept of reduce, reuse, recycle

and recover. When the first three Rs were deemed not suited to the case at hand whether it is based on plastic type or processing cost, the recovery of resources has to be undertaken in a waste to fuel and energy (WtE) manner[11].

Number of strategies have been implemented for the handling of PW including: recycling, landfilling, microbial degradation, energy recovery and incineration [12]. The main WtE processes are thermochemical conversion (TCC), bio-chemical and chemical. The focus of the review at hand is the management and application of PW through TCC processes, namely gasification and pyrolysis. Both processes are relatively more environmental and sustainable compared to incineration technology[11]. Gasification and pyrolysis recover oil, solid residues (char) and combustible gas (syngas)[13]. During treatment, the long polymer chains degrade into shorter ones. As the PW is originally derived from essential petrochemicals and HC, the yielded products are also similar to those in nature. By varying the process conditions such as heating rates, residence time and operating temperature, different product yields can be obtained[14]. Past reviews by Al-Salem et al.[3,13] has described TCC in detail and discussed the most influencing factors on their operation and product yields. The management of PW was also discussed in terms of a hierarchical sequence that puts fuel and energy recovery as the most regarded technologies. Hopewell et al.[4] has also depicted TCC techniques and standards followed for such technologies. In this work, we focus mainly on the energy potential of products obtained from both pyrolysis and gasification; whilst discussing potential real-life applications in industry. This will provide interested stakeholders and environmental authorities a condensed review that fills in future gaps for diversifying energy baskets and delivering solutions for PW accumulation.

The International Energy Outlook report[15] has recently noted that the global energy-related carbon dioxide (CO_2) emissions increase at an average rate of 0.6% per annum between 2018 and

2050. Development of CO_2 utilisation pathways can effectively lower CO_2 emissions. Thermal treatment of PW offers efficient CO_2 utilisation as well as conversion of PW to clean fuel[16],[17]. TCC is a promising long-term solution to PW accumulation, these processes are positioned to assume enormous industrial importance in the near future[18]. **Table 2** depicts a summary of these technologies in comparison to common PW management techniques with emphasis on their main advantages. This article will focus on the recent work and product yields from PW pyrolysis and gasification with an aim to produce fuel and renewable energy streams that could diversify the energy basket of the world and present integration opportunities of such energy for industrial applications. **Table 3** presents comparison between pyrolysis and gasification of PW.

Table 2. Pyrolysis and Gasification Advantages in Comparison to Other Common Waste Management Techniques.

Process	Advantages	Disadvantages
Deposition in Landfill	Low operating and labour cost[19].	Leachate generation containing nitrogen compounds and heavy metal contaminants[19]. Occupation of a large land area[20]. Long decomposition cycle and environment pollution[20]. Restoration of land is not always possible**Error! Reference source not found.**.
Incineration	Suitable for commingled with excessive contamination, separation difficulties or polymer property deterioration[22].	Emitting nitrogen oxides (NO_x) and sulphur oxides (SO_x)**Error! Reference source not found.**.

Process	Advantages	Disadvantages
Pyrolysis	High conversion efficiency and polluting gaseous emissions[Error! Reference source not found.]. Suitable for commingled PW[24]. A wide range of products, liquid, gas, and solid, can be produced from plastic wastes[25].	Moisture content of feedstock affects yield[19]. High cost of operation[19].
Gasification	Flexibility to use different plastics and plastics mixed with other feedstocks, i.e. co-gasification[26]. Fuel syngas generated by gasification is easier to handle, meter, control and burn than solid MSW[27]. Gasification requires considerably smaller fraction of the stoichiometric amount of oxygen necessary for combustion[28]. Gasification takes place in a low oxygen environment which limits the formation of dioxins, SO_x and NO_x[28]. The reducing environment of the gasifier can improve the quality of solid residues, particularly metals[27].	Requires dry feedstock that increases processing cost[20]. In order to use the produced syngas in highly efficient internally-fired cycles (e.g. gas turbines and combined cycles, Otto engines) or to generate high-quality fuels (e.g. diesel, gasoline, hydrogen) and chemicals, the syngas needs to be properly treated - cleaned and conditioned, which is very costly[27].

Table 3. Comparison of Pyrolysis and Gasification of PW.

| Factors	Pyrolysis	Gasification
Main products	Oil, char, gas.	Syngas, ash.
Type of process	Batch or continuous.	
Temperature range	Typically between 450 to 800°C.	> 600°C.
Oxidant	Absent.	Less than required for stoichiometric combustion.

Factors	Pyrolysis	Gasification
Catalyst	May be used to manipulate yields.	Catalyst/steam may be used to manipulate yields.

2. Pyrolysis technology

Pyrolysis involves heating PW in an inert atmosphere to allow the polymer to degrade into small chain HC as well as monomers (primarily alkenes) in a typical temperature range of 450 to 800°C. The pyrolysis process is suitable for mixed PW for the production of fuel and chemicals. It can be used for a singular stream as well (mono-treatment) for polyolefin and polyester plastics[24]. Currently, most of pyrolysis products are applicable to be re-polymerized into plastics in a continuous supply chain process. Pyrolysis is closer to the goal of a cyclic process as it has higher carbon efficiency and alkene products from pyrolysis are better suited for polymerization due to the saturation of the carbon bonds[18]. Generally, pyrolysis is easier to operate as it requires three pieces of capital equipment, the reactor and two separators. Gasification on another hand requires at least five pieces of capital equipment that includes two additional reactors. A generic schematic representing the pyrolysis process is given in **Figure 2** to show the output of a typical pyrolysis process. The reader is referred to **Table 4** for a recent review of successful pyrolytic set-ups for various types of plastics and PW commingled streams.
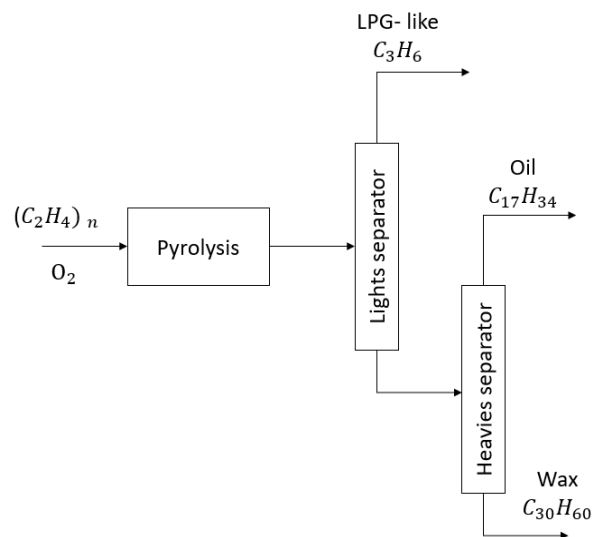
Figure 2. Schematic of Pyrolysis Process. Reproduced from Fox, J. and Stacey, N., 2019. Process targeting: An energy based comparison of waste plastic processing technologies[18]. Copyright 2021 Elsevier.

2.1. Yields and conversion rates

Process conditions of pyrolysis such as temperature, residence type and use of catalyst, all affect the final product yield. For example, operating temperature is important in plastic pyrolysis as plastics degradation occurs at different temperature depending on the chemical structure of the plastics. Temperature influences the cracking reaction of the polymer chains, thus affecting the product distribution. However, catalysts can be used to reduce the temperature required for the pyrolysis process. Pyrolysis experiments results showed that more than 96% recovery of high-quality oil is achievable[6],[24]. Recovered streams have properties very close to liquefied petroleum gas (LPG) and fuel oil. Catalysts reduces the retention time and conversion temperature, and requires less energy than non-catalytic pyrolysis, thereby making the process more economically feasible[29]. Also, catalysts improve the performance of the pyrolysis process and the quality of the pyrolysis product. Gaurh**Error! Reference source not found.** reported that the use of ZSM-5 catalyst reduces the quantity of pyrolysis oil but improved the quality of it. Investigation by Syamsiro et al.[30] revealed that heavy oil fraction ($> C_{20}$) obtained from the pyrolysis of polyethylene (PE) reduces with zeolite catalysts, but the cracking of longer chain to lighter chain hydrocarbons by the catalysts contributes to an increase in the gasoline fraction (C_5-C_{12}). **Table 4** shows the process conditions used by various researchers and their obtained product yields.

2.2. Process mode of operation

Batch processes encompass a closed system with no inflow or out-flow of materials while the reaction is taking place. High conversion in batch reactors can be achieved by leaving the reactants in the system for a longer period of time, i.e.by increasing the residence time. A batch reactor is used for small-scale operation and for testing new processes[31]. However, batch reactors require relatively high labour costs and they involve difficulties with scaling up of the production. Pyrolysis in a batch reactor is usually performed at temperature range of 300-800°C for both thermal and catalytic pyrolysis[1],**Error! Reference source not found.**,[32],[33]. Continuous-flow reactors avoid the problems of batch reactors as they are mainly operated at steady state. Lopez et al.[34] reported that batch process yields higher fraction of heavy liquid while continuous process yields more of light aromatics. The process conditions together with yields for batch and continuous processes are also given in **Table 4**.

2.3. Energy content

Pyrolysis oil (pyro-oil) must be upgraded to reduce sulphur content, improve oxidation stability and to meet fuel standards. Synthesis of liquid fuels from waste is a promising pathway for optimizing waste management towards zero landfilling. However, very few case studies involving commercial-scale plants are available. Faussone[35] conducted a study on commercial plants that pyrolyse plastics from post-consumer recycled materials and directly mine from old landfills to show the feasibility of manufacturing transportation fuels via these methods. Two pyrolysis plants – located in South East Asia and Eastern Europe were studied. The plant located in South East Asia is a semi-continuous pyrolyser with the capacity of 5-7 tons/day of feedstock. The middle and heavy cuts from the distillation of produced pyrolysis oil were almost within the limits set by the EN590 and ISO8217 standards. Plant in the Eastern Europe employs a batch design for pyrolysis of plastic and tires with capacity of 5–10 tonnes per day. The final boiling point (FBP)

of the pyro-oil obtained from the plant was high due to the dissolved wax and sulphur content. This makes it not appropriate as a fuel for transportation application. However, as the fuel is for power generation, only the sulphur content needs to be kept under 1000 ppm, hence the target was met. This case proves that if the quality of the produced fuel does not meet transportation standards, it can still contribute to the circular economy and be used as a substitute for fossil fuel. Miandad et al.[36] and Syamsiro et al.[30] also showed that the properties (e.g. viscosity and heating value) of pyro-oil obtained from their investigated plastic wastes were close to the properties of conventional diesel. Plastic wastes and the resulting oil and gas from their pyrolysis have high energy contents. Different authors report different ranges of calorific value (CV) of obtained syngas and pyro-oil.

Khan and Kabir[11] mentioned that the syngas produced through pyrolysis has calorific value of 10-20 MJ/Nm^3 and is suitable for fuel production. Papuga et al.[37] stated that pyro-oil has high heating value (45.9603 ± 0.15 MJ kg^{-1}), which is close to the heating value of high quality coals (43 MJ/kg), and crude oil (44 MJ kg^{-1}). Zhang et al.[38] performed analysis of H/C ratio, and HHVs of liquid oils. The hydrogen contents in the oils produced from PP and PE pyrolysis were found to be 12.5 % and 11.8 %, respectively. The increased hydrogen content in the oils results in a higher H/C ratio, thus improving the HHV of oil. Demirbas[39] showed that the pyro-oil obtained from mixed plastic waste containing PE, PP, and PS has a high energy content (44.1 MJ kg^{-1}). Miandad et al.[36] reported that oil produced from the pyrolysis of PS, PP and PE have heating values in the range of 41.4 - 41.8 MJ kg^{-1}and this range is close to that of conventional diesel (43.06 MJ kg^{-1}). Jiang et al.[40] showed that the energy recovered from the combustion of the non-condensable gases obtained from the molten solar salt pyrolysis of mixed plastic waste (MPW) is higher than the energy required for the pyrolysis. They reported that 605 kW was required for the pyrolysis of 8000 t yr^{-1} of MPW whereas 662 kW of electricity was generated from the non-condensable gases.

Table 4 reports the energy content values of pyrolytic oil obtained by different process conditions reported by various researchers. The studies reviewed used different feedstock (PE, PS, PET, PP) and operating conditions with temperature ranging from 410 to 700°C and residence time 30 to 120 minutes. As can be seen the reported values of energy content range from lowest 41.10 to 46.16 MJ kg^{-1} which are very close to the heating values of conventional fuels. It also seems that operating conditions do not have a significant effect on the energy content of pyrolytic oil. Quesada et al.[41] carried out pyrolysis of polyethylene film under different operation conditions in order to determine if the quality of the fuel depended on them. The study showed that the properties of obtained fuel did not change with operating conditions used and that the chemical and physical characteristics of the obtained oils were similar to those of commercial fuels (gasoline and diesel).

Table 4. Pyrolysis of PSW: Process Conditions, Yields and Energy Content.

Plastic Type	Treatment	Temperature	Residence Time	Energy Content	Yield	Reference
HDPE	Pyrolysis followed by distillation	Reactor with two heating zones (420 and 440°C)	2 hrs	46.16 MJ kg^{-1}-liquid fraction	Oil 74%, Solid residue 17% and gas 9%	[42]
PE and PS	Pyrolysis using fixed bed pilot reactor	410-450 °C			Lighter fractions with yields of 16-89%	Error! Reference source not found.
PP 45% LDPE 35% HDPE 25%	Pyrolysis using fixed bed pilot reactor	500 °C	45 min	45.96 MJ kg^{-1}-liquid fraction	Oil 32.80%, gas 65.75%, and the solid 1.46%	[37]
	Pyrolysis using fixed bed pilot reactor	525 °C	45 min	45.96 MJ kg^{-1}-liquid fraction	Oil 28.80%, gas 69.98%, and the solids 1.23%	
	Pyrolysis using fixed bed pilot reactor	500 °C	90 min	45.96 MJ kg^{-1}-liquid fraction	Oil 30.37%, Gas 68.17%, and the solid 1.47%.	
PE	Pyrolysis in batch autoclave reactor with nitrogen	500 °C	60 minutes		Oil 93 wt% and gas 7 wt%	Error! Reference source not found.
PE		500 °C	60 minutes		Oil 95 wt% and gas 5 wt%	
PS		500 °C	60 minutes		Oil 71 wt%, gas 2 wt%, solid 27wt%	
PET		500 °C	60 minutes		Oil 15 wt%, gas 32 wt%, solid 53wt%	

Plastic Type	Treatment	Temperature	Residence Time	Energy Content	Yield	Reference
HDPE 58.6% LDPE 26.9% PP 5.6% PS 8.8%, other thermosets 0.1%	Slow pyrolysis in a batch reactor	500°C non-isothermal heating condition with heating rate of 10°C/min		42.30 MJ kg^{-1}-Liquid fraction	Oil 75.8 wt%, Gas 14.2 wt% and char 10 wt%	
	Slow pyrolysis in a batch reactor	500°C heating condition with heating rate of 10°C/min in a bath reactor		41.10 MJ kg^{-1} - Liquid fraction	Oil 82 wt%, Gas 10.5 wt% and char 8.5 wt%	[14]
	Fast pyrolysis	500°C Isothermal heating condition with heating rate of 20°C/min			Oil 7 wt%, Gas 91 wt% and char 2 wt%	
PE	Thermal pyrolysis in a batch reactor	700°C	30 min	45.95 MJ kg^{-1} - Liquid fraction	Oil 68.02 wt%, Gas 16.82 wt% and solids 15.16 wt%	**Error! Reference source not found.**
PE	Catalytic pyrolysis in a batch reactor using ZSM-5 catalyst	700°C	30 min	46.00 MJ kg^{-1} - Liquid fraction	Oil 72.72 wt%, gas 21.22 wt% and solids 6.06 wt%	
PE				Oil's HHV: 45.45 MJ kg^{-1}	Oil 41.15%, gas 51.95%, and char 6.9%	
PE 60% PP 40%	Catalytic pyrolysis in a batch reactor using zeolite catalyst	Pyrolysis at 500°C and catalytic reforming at 450°C.		Oil's HHV: 44.53 MJ kg^{-1}	Oil 42.40%, gas 53.93%, and char 3.67%	[45]
PE 50% PP 40% PS 10%				Oil's HHV: 42.57 MJ kg^{-1}	Oil 45.13%, gas 51.40%, and char 3.47%	

Plastic Type	Treatment	Temperature	Residence Time	Energy Content	Yield	Reference
PE 50% PP 30% PS 5% PET 10% Others 5%				Oil's HHV: 44.26 MJ kg^{-1}	Oil 43.40%, gas 50.67%, and char 5.93%	
PS					Oil 80.8%, gas 13.0%, char 6.2%	
PE	A 20 L pilot scale pyrolysis reactor				Oil 42.0%, gas 54.5%, char 3.5%	
PP					Wax 25.0%, gas 62.0%, char 13.0%	
PS 50% PP 50%	A 20 L pilot scale pyrolysis reactor				Oil 25.0%, gas 69.9%, char 5.1%	
PS 50% PE 50%	A 20 L pilot scale pyrolysis reactor	450ºC	75 min	41.4-41.8 MJ kg^{-1}	Oil 54.0%, gas 38.3%, char 7.7%	[36]
PP 50% PE 50%	A 20 L pilot scale pyrolysis reactor				Oil 24.0%, gas 51.2%, char 24.8%	
PS 50% PE 25% PP 25%	A 20 L pilot scale pyrolysis reactor				Oil 49.0%, gas 47.1%, char 3.9%	
PS 40% PE 20% PP 20% PET 20%	A 20 L pilot scale pyrolysis reactor				Oil 40.0%, gas 42.0%, char 18.0%	

3. Gasification technology

Gasification, or in other words "indirect combustion"[27], is an endothermic thermal conversion process which can convert any carbonaceous fuel into syngas, a mixture primarily comprised of hydrogen (H_2) and carbon monoxide (CO) in the presence of oxidant amount lower than that for the stoichiometric combustion. Syngas is the building block for many fuel and valuable chemicals. It can be transformed into commercial products such as transport fuels, fertilisers, chemicals or used as a substitute to natural gas[46]. In light of this, gasification presents an attractive alternative process for clean energy production from PW. The waste gasification is a multipart process that occurs at a temperature above 600°C. Gasification is classed based on the oxidising agent: oxygen gasifiers, steam gasifiers, air-blown gasifiers, or the heat source: auto-thermal or direct ones, along with allo-thermal or indirect gasifiers[46]. In addition to utilising air/oxygen as a gasification agent, CO_2, steam, and electrically generated plasma may be used. Several studies considered supercritical water (SCW) gasification technology as well[20],[47]. SCW achieves high efficiency and clean energy thanks to provision of high reaction rate and homogeneous reaction medium for the decomposition of HC[20]. Bungay[48] utilised ultra-high purity N_2 and CO_2 gas along with air to provide a way to oxidise the remaining char and combustibles in his samples. In most common gasification process, there are four main stages as depicted in **Figure 3**.
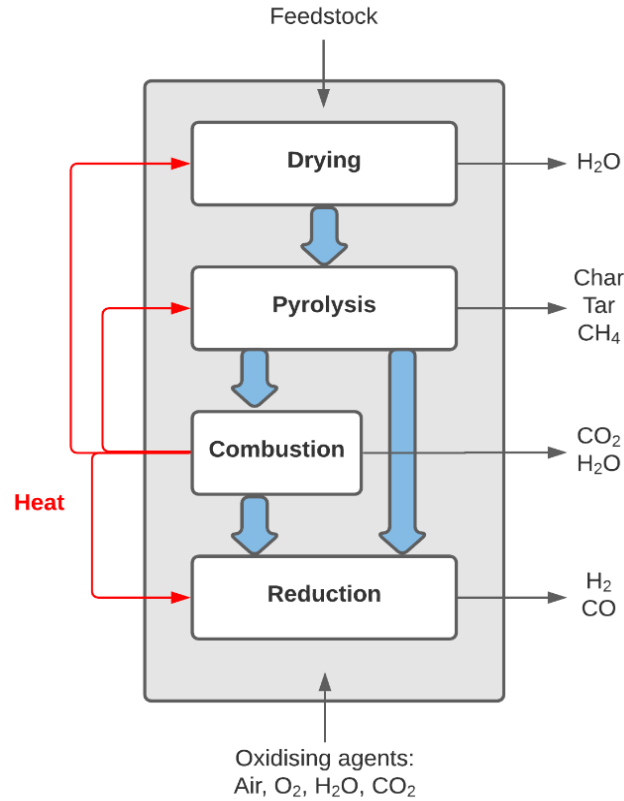
Figure 3. Main General Gasification Processes. Reproduced from Clifford, B. C., 2018, 4.3 Gasification[49]. Public Copyright License 2021.

A remarkable advantage of gasification compared to pyrolysis is its flexibility to jointly valorise plastics of different composition or mixtures or plastics mixed with other feedstock (i.e. co-gasification with biomass). The composition, and therefore applications, of the gas produced depends on process parameters including the gasifying agent and its flow rate, plastic properties and feed rate, operating temperature and pressure[26],[50]. With their high reactivity and gasification rate, plastic wastes can be converted in a low-temperature gasification system. Gasification has a benefit of combining the operating conditions (e.g. equivalence ratio and temperature) and the attributes of the particular reactor (fluidized bed, fixed bed, entrained bed, moving grate furnace, vertical shaft, rotary kiln, plasma reactor, etc.) to produce a syngas suitable for use in various applications. It can be utilised as a fuel gas that can be combusted in a conventional burner,

connected to a boiler and a steam turbine, or in a more efficient energy conversion device, such as gas reciprocating engines or gas turbines[27].

3.1. Yields and conversion rates

The main product of gasification is syngas. Usually, it is contaminated by undesired products such as particulate, tar, alkali metals, chloride and sulphide. A significant amount of char is typically produced during gasification which needs to be further processed and/or burnt[1]. Part of fuel produced is combusted to provide the heat needed to gasify the rest in autothermal gasification, in case of air gasification the energy is supplied by an external fuel source [27].

Manipulation of various factors during the gasification process, such as feedstock concentration, oxidising agent, temperature, or time results in different qualities of the produced syngas. In their optimization study, Chen et al., [51] have found that air gasification favours H_2 generation with use of moderate equivalence ratios. Using steam as an oxidizing agent, H_2 and CO yields are higher with elevated temperature. It is however the catalytic-steam gasification (NiO/-Al_2O_3 or $K2CO_3$) that not only increases the H_2 production, but also decreases char and tar yields[51]. Bai et al.[47] studied the performance of polypropylene (PP) plastic in supercritical water. It was found that PP reaches low values of carbon efficiency ($\approx$ 64%) at 800 °C which was justified by low oxygen content making it difficult for PP to form a gaseous product. The process of gasification was later optimised by modifying two main factors, temperature and residence time. The optimal conditions were found to be 750°C and 60 min which yielded 72.32 wt% of carbon conversion. Alvarez et al.[52] also mentioned that the reduction in CO and CO_2 from 35.5 vol.% to 27.5 vol.% and 15.7 vol.% to 11.2 vol.% respectively with the increase in the fraction of PP in the co-gasification of PP and sawdust was attributed to the low oxygen content in PP. On the contrary, hydrogen fraction was enhanced with more PP in the feed as PP, which is a polyolefinic plastic, increases the

hydrogen to carbon molar ratio (H/C) of the feed[52]. Similar observation was reported by Pinto et al.[53] for the co-gasification of wood pine and PE. The importance of feedstock properties on product distribution was also reported by Wu and Williams[54]. They showed that gas yields from the pyrolysis-gasification of polystyrene (PS), high density polyethylene (HDPE) and PP were 11.6 wt.%, 53.5 wt.% and 59.6 wt.%. PS had the lowest gas yield due to the high energy required for cracking its gaseous products. Another good example of the effects of feedstock properties can be derived from PVC as the gasification of the material will potentially lead to the formation of HCl due to the high chlorine content in the feedstock. Zaccariello and Mastellone[55] studied the influence of fuel composition on air gasification performance by performing mass and energy balances on a pre-pilot scale bubbling fluidized bed reactor fed with mixtures of wood, coal and plastic waste. The composition of fuel clearly affects the characteristics of the gas produced during the gasification process. Whilst the CO_2 content is similar in cases of gasification of purely recycled plastic (RP), plastic mixed with virgin wood (WRP), and plastic mixed with virgin wood and coal (WRPC), it was found that feedstocks containing woody biomass yield more hydrogen and carbon monoxide, and less methane and other light hydrocarbons[55]. Similar approach of co-gasification of plastics with biomass has been studied by other researchers. The reaction temperature is an operating parameter that is worthy of being mentioned. The parameter strongly influences the gasification process. It has been reported that an increase in the reaction temperature promotes gas-solid reaction, enhances tar cracking, char conversion, and gas yield. However, it reduces the fraction of methane and heavier hydrocarbons and, in association, the heating value of the resulting syngas[56]. It is also possible to utilise a catalyst during gasification process which may modify the yields of the products. Wu et al.[57] have tested gasification of polypropylene with

use of Ni/Ca-Al and Ni/Zn-Al catalysts under steam as the oxidising agent, which resulted in hydrogen-rich syngas (over 60 vol%).

3.2. Batch and continuous processes

As previously explained, a batch process is a closed system with no inflow or outflow of materials while the reaction is taking place. Manipulating parameters such as temperature or residence time may increase the efficiency of the reaction and yield higher conversion. Gasification, just like any other thermal process, is typically a continuous process[28]. Batch processes are used for testing new technologies, as it was done by Bai et al.[20],[47]. In their study, they performed gasification using a quartz tube reactor with SCW as the gasifying agent. De Filippis et al.[28] describes two batch gasification system that have a potential for commercial success. These are Brookes Gasification Process and Molecular Dissociation. The Brookes Gasification Process is suitable for processing a wide range of feedstock materials, including PSW, however it is not suitable for treating large amount of MSW. The Molecular Dissociation was designed for thermal treatment of small amounts of untreated waste and it ensures nearly 100% burn-out of the waste and the by-product ash with minimal residual carbon[28]. For more common continuous processes of gasification, different types of reactors may be used. They are classified as fixed/moving bed, fluidised bed, and spouted bed gasifiers[50]. **Figure 4** presents schematics of most common types of gasifiers. Regardless of the gasifier type, the steps involved in gasification include drying, devolatilization (pyrolysis), combustion, and gasification (reduction) as depicted in **Figure 3**.
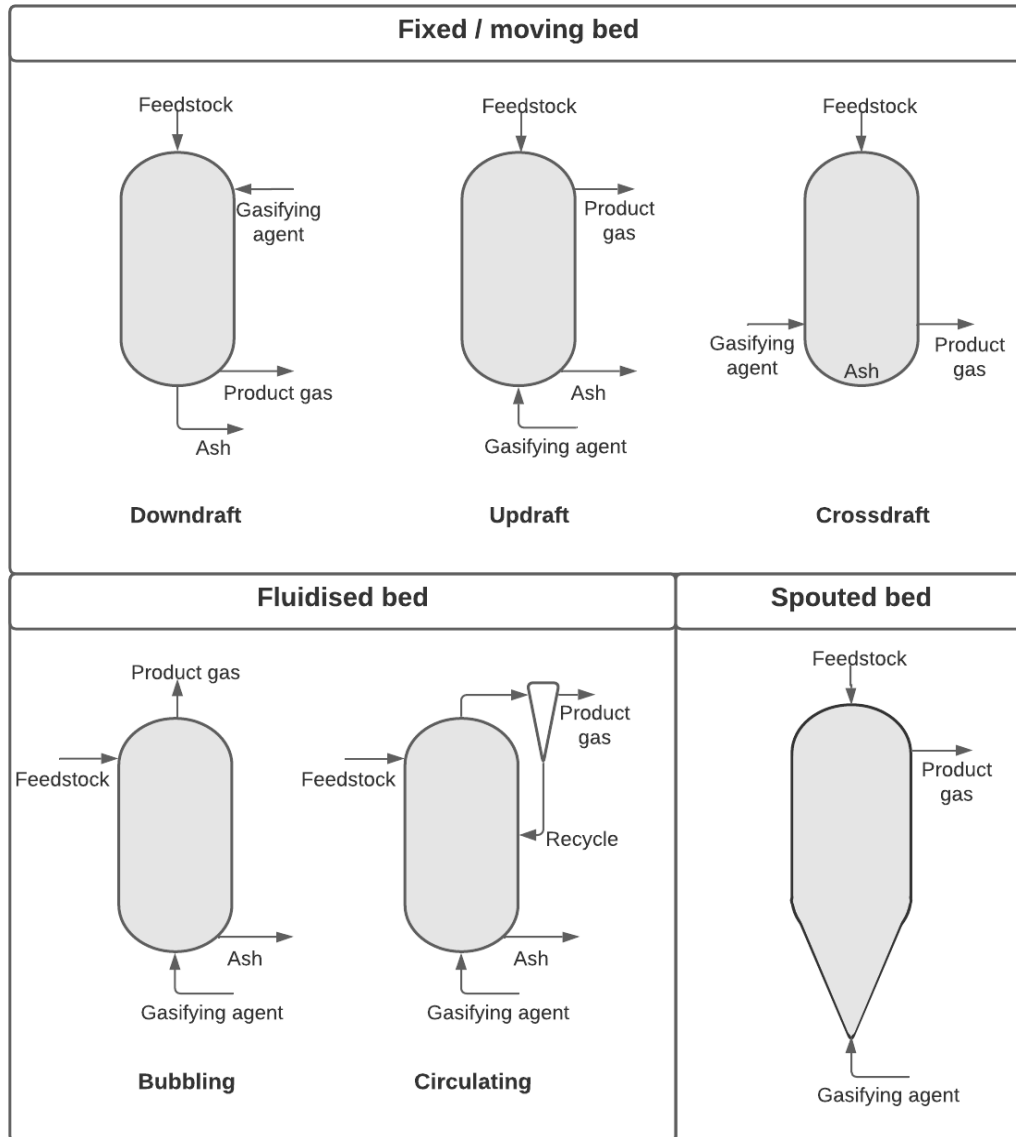
Figure 4. Conventional Continuous Gasifier Types. Reproduced from Salaudeen, S. A., Arku, P., Dutta, A., 2019, Gasification of Plastic Solid Waste and Competitive Technologies[50]. Copyright 2021 Elsevier.

3.3. Energy content

The partial oxidation with air produces a diluted gas with nitrogen up to 60% with CV around 4-7 MJ/m³ N. This value is considerably lower than that of natural gas with the value of 38 MJ/m³ N. The oxygen enriched air has the ability to produce a syngas with higher heating value. The

partial oxidation with pure oxygen generates a syngas with a higher calorific value, ranging between 10 and 15 MJ/m^3 N. The steam gasification generates a high hydrogen concentration, medium heating value (15–20 MJ/m^{3}N) and a nitrogen-free syngas[27]. Some plastics like polyethylene (PE), polypropylene (PP), or polystyrene (PS) have high calorific values of ~40 MJ/kg, which makes them attractive for use in waste to energy applications. Janajreh et al.[58] have found that mixtures of different types of plastic (namely LDPE, PP, and PS) provide with a similarly high calorific value as individual plastics, and furthermore give the highest cold gasification efficiency (CGE) which implies that there is potential for eliminating the need to segregate the PW before it is treated. CGE is defined as the ratio between the chemical energy of the produced syngas and the chemical energy of the waste fed to the process[27].

Zaccariello and Mastellone[55] experimented on co-gasification of plastics with different types of biomass. They attribute synergistic effects to interaction between the produced volatiles themselves, or between volatiles and the ashes produced during gasification of biomass. In their research, they found that recycled plastic accompanied by virgin wood yields a higher energy content than the recycled plastic itself. Although co-gasification of plastic waste and biomass may appear attractive, it is difficult to predict if this is always the case. In another co-gasification study, the highest energy content was obtained through gasification of pure plastics. Presence of biomass within the feedstock (namely Acacia) reduced its gross calorific value[60]. **Table 5** reports the energy content values of syngas obtained by different process conditions and feedstocks reported by various researchers.

Table 5. Gasification of PSW; process conditions, yields and energy content data.

Plastic Type	Treatment	Temperature	Residence Time	Energy Content	Yield	Reference
Powdered PP 10 wt% formic acid solution	Supercritical water (SCW) batch gasification using quartz tube reactor	750 °C	60 min		Gas 79.86 wt% carbon conversion: 51% CH_4, 28% H_2, 19% CO_2, 2% CO	[47]
HIPS	Supercritical water (SCW) batch gasification using quartz tube reactor	800 °C	60 min		Gas 94.48 wt% carbon conversion: 20 wt% H_2, 12.5 wt% CO_2, 7.5 wt% CH_4, 1 wt% CO	[20]
Recycled plastic (mixed)	Continuous gasification in bubbling fluidised bed reactor (pre-pilot scale)	877°C		22.77 MJ kg^{-1}	Gas mixture (CO_2, CO, H_2, CH_4, C_3H_m) and ash 0.84 ± 0.11 carbon conversion	[55]
Plastic Waste and Virgin Wood		872°C		23.84 MJ kg^{-1}	Gas mixture (CO_2, CO, H_2, CH_4, C_3H_m) and ash 0.83 ± 0.22 carbon conversion	
LDPE	Drop tube reactor	50 °C for 2 min, ramped to 700°C at fixed heating rate of 5, 10, 15 and 20 °C/min, and finally left in isothermal condition for 5 min	43.363 MJ kg^{-1}± 0.251 CGE: 59%	Syngas	[58]
PP			40.965 MJ kg^{-1}± 0.235 CGE: 63%	Syngas	

Plastic Type	Treatment	Temperature	Residence Time	Energy Content	Yield	Reference
PS				40.985 MJ kg^{-1} ± 0.212 CGE: 73%	Syngas	
60% LDPE 25% PP 15% PS				42.407 MJ kg^{-1} ± 0.212 CGE: 89%	Syngas	
PE	Equilibrium modelling with Aspen Plus	900ºC	Equilibrium model	38.04 MJ kg^{-1}	LHV of syngas: 11.36 MJ/Nm^3 H$_2$/CO: 2.1	[59]
Recycled PE	Fluidized bed reactor	850ºC		45.5 MJ kg^{-1} CGE: 45% CCE: 57%	LHV of syngas: 6.3 MJ/Nm^3 7.8% H$_2$, 5.0% CO, 8.7 CO$_2$, 8.7% CH$_4$, 66.9% N$_2$	[61]
PE	Spouted bed reactor	900ºC		PE HV: 43 MJ kg^{-1} CCE: 91% Gas HV: 15.5 MJ kg^{-1}	Gas yield: 178.7 g/100g of plastic 60.3% H$_2$, 28.2% CO, 1.4% CO$_2$, 7.2% CH$_4$	[56]

Plastic Type	Treatment	Temperature	Residence Time	Energy Content	Yield	Reference
Sawdust with 20% PP	2-stage fixed bed reactor with and without Ni/Al$_2$O$_3$ catalyst	600°C for pyrolysis and 800°C for gasification			Gas yield: 56.9 – 85.0 wt%	[52]
Sawdust with 20% HDPE					Gas yield: 59.9 – 77.5 wt%	
Sawdust with 20% PS					Gas yield: 50.9 – 68.1 wt%	
PE	Equilibrium modelling with Aspen Plus	Adiabatic reactor with a heat duty of zero	Equilibrium model	22.07 MJ kg^{-1}	For PE/PET blend, Syngas efficiency: 28% - 70%	[62]
PET				22.07 MJ kg^{-1}	LHV of syngas: 5 – 10 MJ/Nm^3	
PP	Fluidized bed reactor	703°C – 915°C (ER of 0.2 – 0.45)		44.7 MJ kg^{-1}	Gas yield: 76.1 – 94.4 wt% HHV of gas: 11.3 – 5.17 MJ/Nm^3 Char yield: 15.9 – 5 wt%	[63]
PE	Catalytic-steam gasification	700°-900°C	Continuous process		36.98 mol% H$_2$, 27.37 mol% CO, 20.78 mol% CO$_2$, 9.94 mol% CH$_4$	[51]

The past review of Sharuddin et al.[32] focused on discussing the product yields of pyrolysis namely in catalytic operation. There also exists another detailed review articles published previously detailing advantages of pyrolysis and gasification[3-4,13]. In this work we have also detailed the energy potential of both technologies and their products, and we also detail their real-life industrial application within the next sections.

4. Integration to energy systems, energy grids and turbines

Chemical recycling technologies can play an important part in the shift towards closed-loop recycling of materials and circular economy. They create the opportunity to handle challenging waste streams such as hazardous materials. Pyrolysis allows PW to be valorised into valuable fuel and monomers[64]. Several works have studied integration of the pyrolysis and gasification into the energy systems and use of the produced synthetic oil and gas in engines, turbines etc. However, Pyrolysis liquid tends to be thermodynamically unstable and re-polymerises. Thus, post treatment of liquid is required to retain its quality over prolonged period. The stability and ageing properties of pyrolysis oils determine its quality and therefore its applicability in the energy sector[64]. The CV, physical properties and the chemical structure can be improved with the post treatment of pyrolytic oil with processes such as de-moisturizing, de-sulphurisation, and distillation[65].

4.1 Feasibility of integration

Mastellone[66] demonstrated that the integration of pyrolysis and gasification of PW coupled with a mechanical sorting is energetically and technically feasible. The studied system aimed to recover the greatest amount of materials and energy from PW and the studied process is given in Figure 4. The calorific value of syngas calculated by the energy balance was 5588 MJ t^{-1} (about 7 MJ/Nm^3). The usage of an engine to burn syngas, permits the conversion of chemical energy into heat and electricity by co-generation, generating power of 11.7 MW. The produced gas has the

calorific value of 43 MJ/kg. The engine for heavy fuel gas (LPG) allows conversion of 9.3 MW

chemical energy into electricity and heat by co-generation, generating electrical power of 3.3 MW.
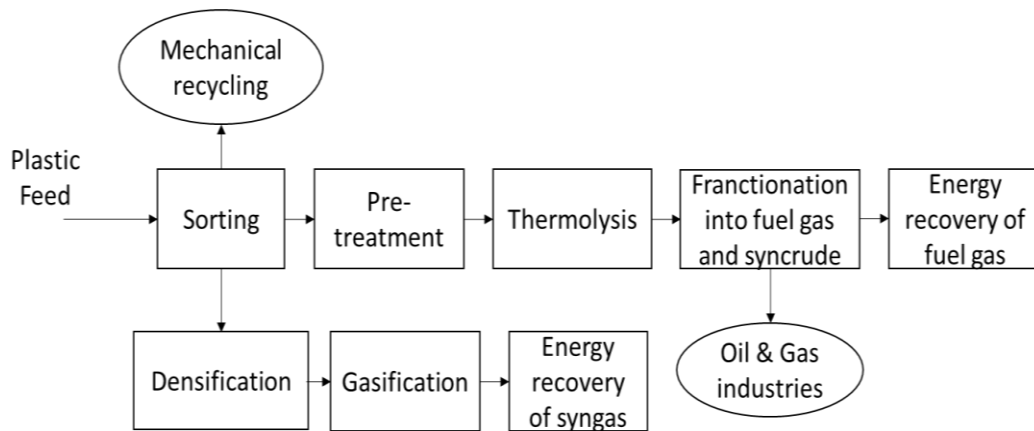
Figure 5. Process under Study. Reproduced from Mastellone, M., 2019. A feasibility assessment of an integrated plastic waste system adopting mechanical and thermochemical conversion processes[66]. Copyright 2021 Elsevier.

Dong et al.[67] conducted a life cycle assessment (LCA) using theoretical analysis and a case study of commercial plants. The study involved gasification, pyrolysis, and incineration as well as energy utilisation; gas turbine/combined cycle, steam cycle, internal combustion engine. The theoretical analysis showed that gasification and pyrolysis coupled with a gas turbine/combined cycle, have the ability to reduce the environmental loadings. The benefits arise from an improved energy efficiency leading to a decrease in fossil fuel consumption, and the lowered process emissions by syngas combustion. The produced syngas can also be utilised in a gas turbine or an internal combustion engine. Potentially, the electrical efficiencies would be 35.5% for gas turbine and 25.0% for engine. Ortiz et al.[68] designed a process considering material and energy integration, which consists of fast pyrolysis of MSW to produce bio-oil. The potential economic profitability of the plant was also examined, and it showed that for a feeding of 50 t/h of MSW reject fraction, a generation of a net power equal to 10.65 MWe and a production of 5.2 t/h biofuels

may be achieved, as a result achieving a very low gate fee (16.7 €/t). Thus, the process seems economically feasible.

4.2 Application of Pyrolysis oil

Kalargaris, Tian and Gu[69] obtained pyrolysis oil via fast pyrolysis of mixed plastic. The obtained oil had comparable properties to conventional fuel (diesel). Blends of pyrolysis oil with diesel ranging from 0% to 100% were tested on a four-cylinder direct injection diesel engine at various engine loads, 25% to 100%. It was found out that at high loads the engine performed in a similar way to diesel. However, lower loads had stability issues caused by the longer ignition delay period. At full load, the brake thermal efficiency was slightly lower for pyrolysis oil, but NOx emissions were higher. The study showed at certain operation conditions pyrolysis oil can be a promising alternative to conventional fuel.

In a catalytic operating mode, Miandad[70] studied pyrolysis and showed that 70-80% of PW can be converted into pyro-oil that has similar characteristics to conventional diesel fuel that can be used in transport fuel and electricity generation. Ghenai et al.[65] conducted batch pyrolysis reaction with polyethylene, polystyrene, and polypropylene. The physical and chemical characteristics of the produced pyrolytic oil were compared with diesel fuel. The heating values of obtained pyrolytic oil were 77% to 85% of the gross CV of diesel fuel. The treated pyrolysis oil can be used in compression ignition engine as an alternative to diesel. Ghenai et al.[65] also modelled the grid-tied solar PV system for the pyrolysis reactor to study its performance. The proposed system was analysed to be economically viable (86 $ MWh^{-1}) and was found to produce low greenhouse gas emissions (162 kg CO_2 MWh^{-1}).

Saptoadi and Pratama[45] indicated that pyrolysis oil can partially substitute kerosene as energy source. They investigated the performance of pyro-oil (from PE, PP, PS, and PET) mixed with kerosene as fuel in cooking stove and obtained thermal efficiency in the range of 47.5% - 51.1% for the mixture. The obtained efficiencies were very close to the thermal efficiency obtained from the use of pure kerosene (i.e. 53.08%). It is noteworthy that the quality of pyro-oil from plastic waste can be upgraded by treatments such as the removal of particles, pollutants, water, and acids as required for various applications.

Phetyim and Pivsa-Art[71] studied the co-pyrolysis of PW (PP, HDPE, PS) with used lubricant oil to produce a fuel similar in properties to diesel fuel. A semi-batch process was used with the process temperature of 450°C. It was found that the oil produced using an Oil:HDPE:PP:PS ratio of 50:30:20:0 exhibited properties similar to the diesel fuel. The comparison of obtained pyrolysis oil to the standard diesel specification is given in the **Table 6**. In order to conform with said market standards, pyro-oil is typically treated using calcium hydroxide to effectively reduce sulphur content from oil. This will also alter the energy content as such. **Table 6.** Properties of obtained pyrolysis oil by Phetyim and Pivsa-Art[71] compared to standard diesel oil as specified in BS EN 590:2013 Diesel Fuel Specification[72].

Properties	Obtained Pyrolysis Oil	Standard Diesel Oil
Flash point °C	37	>55
Viscosity cSt at 40 °C	5.84	2-4.5
Specific gravity	0.82	
Density at 15 °C kg/m^3		820-845
Distillation °C at 90% recovery	373	
Distillation °C at 95% recovery		<360
Colour	4.5	

Properties	Obtained Pyrolysis Oil	Standard Diesel Oil
Cetane index	67	>46

Pyrolysis of plastic into fuel oil, gas and char is a valuable recovery process as well. As demonstrated several researchers managed to obtain pyrolytic products with high heating values and properties similar to the conventional fuels such as diesel. Such resource recovery also reduces the problem of disposal of plastic waste which provides additional environmental benefit. The oil derived from recovery of plastic waste can be utilised in internal combustion engines to produce heat and power.

4.3 Application of Syngas

PW is abundant and has high heating value due to which it is an ideal source of energy. The main product of gasification, syngas is a valuable resource. After appropriate treatment, syngas can be used directly in highly efficient internally-fired cycles, such as gas turbines or Otto engines[27]. The treatments necessary to ensure the required quality of syngas include particulate removal (e.g. dry gas cleaning, cyclone separators, barrier filters) and tar removal (e.g. granular beds, electrostatic precipitators, scrubbers)[73]. Syngas can also be used as in the Fischer-Tropsh synthesis to produce high-quality fuels like diesel, gasoline, hydrogen[27] or to produce other chemicals, e.g CO hydrogenation to yield methanol[74]. It must be noted that syngas intended for chemical syntheses is required to be cleaned up more rigorously than syngas intended for use in turbines or engines[73]. A wide range of applications of syngas makes the gasification process an appealing method of waste management. As studied by various researchers, mixed plastic waste can be fed into gasification process which brings additional economic benefit of removing the need to sort the plastics prior to the process. Lee et al.[75] converted MPW in their developed 500 kWth

moving-grate gasifier and tested the power generation potential of the produced gas, which contains mainly H_2, CO, CO_2, and CH_4, in a 30 kWe gas engine. Although the producer gas contained significant amount of tar, they achieved clean gases with the combination of flame-assisted tar reformer and gas cleaning process with bag filter, gas cooler, and scrubber. With their optimal operating condition (excess oxygen ratio, ER of 0.3 – 0.4), they obtained a power output above 20 kWe and a power generation efficiency of around 22%.

.

5. Real world applications

Gasification and pyrolysis technologies used for the thermochemical conversion of PW into more valuable products, such as fuels, waxes, fertilisers and other chemicals have been implemented on industrial scales in several parts of the world. Vadxx[76] used TCC technologies to actively reduce the waste sent to landfills, incinerators and water eco-systems by converting plastic waste to a range of energy products, such as diesel stock, naphtha, synthetic natural gas. Japanese waste plastics liquefaction plant, operated by Sapporo Plastics Recycling, uses pyrolysis process pre-empted by dechlorination process to produce a wide range of hydrocarbons (light, medium, and heavy oils) and various by-products[77]. Brightmark is currently constructing their plastics renewal facility in Indiana, US, which will have a capacity to convert 100,000 tons/year of PW into 18 million gallons of ultra-low sulphur diesel fuel and 5 million gallons of wax[78].

Gasification of plastics has been studied as early as 1970s[1]. However, it has not yet been popularised commercially; gasification of other materials on the other hand is well known since the 19th century. Texaco and Shell's entrained-flow coal gasification has been recognised as one of the leading clean coal technologies, thanks to its large capacity, coal adaptability, high carbon conversion and variable load ability[79]. Based on Texaco's gasification process, a pilot scale experiments with PW were carried out in the US. Prior to gasification with oxygen and steam at 1200-1500°C, the PW is mildly thermally cracked. After a range of cleaning processes, a dry syngas is obtained, mainly consisting of CO and H_2 and low quantities of CH_4, CO_2, H_2O and inert gases[1]. The Secondary Raw Materials Centre SVZ Schwarze Pumpe GmbH is another real-life example of gasification technology which uses a combined plant for the recycling and conversion to energy of hydrocarbon-containing wastes. It utilises the combined gasification of waste together with coal in a plant formerly designed for fixed-bed pressure gasification of brown and hard

coal[80]. In Italy, a Molecular Dissociation pilot plant has been designed and constructed as part of Belvedere S.p.A. landfill. The plant works with unsorted MSW[28] to convert it into syngas. The Syngas is combusted in an afterburner, at a temperature of about 800°C, that is connected to a thermal energy recovery system[81]. Waste Gas Technology UK Limited (now dissolved) has developed a process in which various waste types (MSW, PW, sludges, ELTs) are dried out, mechanically treated, sorted, granulated and finally fed into a reactor for gasification at 700-900°C to produce gas. A plant with the capacity of 500 kg/h sewage sludge was established by the licensee OSC Process Engineering Ltd. in South Wales in 1998 for Welsh Water at Nash Water Works mainly to fire the dryer. A 110 kg/h unit was also installed in France in 2000[1].

6. Challenges and Perspectives

Synthesis of fuels from waste is a promising pathway for improving waste management and shifting it towards zero landfilling. The main challenges associated with pyrolysis and gasification of PW are inconsistency in feedstock and final products, plastic waste sorting and unclear regulations. Possible solutions could be cooperation between feedstock providers, sorting of plastics for cost-effective recycling. Qureshi et al.[64] reported that one of the challenges are complexity of the legislative framework for pyrolysis of plastic waste. If pyrolytic oil is used as a fuel, the GHG savings criteria set out in the revised Renewable Energy Directive (2018/2001/EU) needs to be fulfilled. According to the Waste Framework Directive WFD 2008/98/EC 'recycling' involves any recovery process by which materials are reprocessed into products, materials or substances whether for the original or other purposes. It does not include energy recovery or using products as fuels. Thus, one of the challenges is that pyrolysis is not considered to be recycling process under EU legislation, if its end product is utilised for energy production. Qureshi et al.[64] highlight that this status should be changed to allow pyrolysis to develop into a feasible business.

 Another challenge and research gap is that very few case studies involving commercial-scale plants are available. The economic assessment of the commercial pyrolysis operation is needed, and more information and studies on the feasibility of process scale up.

7. Conclusions

Plastics possess numerous benefits to society. However, as the global population grows, the generation of plastic waste (PW) grows with it at a proportional manner. PW is made of different hydrocarbons (HC) and stores substantial amount of chemical energy which can be recovered to meet energy demand. Sustainable waste management remains a major challenge nowadays. One of the strategies to handle PW is its conversion/recovery. This paper concentrated on the pyrolysis and gasification treatment of PW and depicted a summary of these technologies in comparison to common PW management techniques with emphasis on their main advantages. These treatment techniques can be used to process mixed plastic waste (MPW) without a need to separate them, improving economic benefit of the process by eliminating the cost of sorting the PW. This article focused on the recent work and product yields from PW pyrolysis and gasification with an aim to produce fuel and renewable energy streams that could diversify the energy basket of the world and present integration opportunities of such energy for industrial applications. Fuel synthesis from PW is a promising route for optimising waste management towards zero landfilling. However, limited amount of case studies involving commercial-scale plants are available. Researchers report various ranges of calorific value (CV) of obtained syngas and pyrolytic oil, some of them being close to that of the conventional fuel. If the quality of the obtained fuel does not meet transportation standards, it can still be effectively used as a substitute for conventional fuel after appropriate treatment and thus contribute to the transition towards circular economy. The studies of possible integration into energy systems have shown that pyrolysis and gasification have the potential to lessen the environmental loadings and are promising alternative fuel. The benefits arise from an improved energy efficiency leading to a decrease in fossil fuel consumption, and the lowered process emissions. The produced fuel can be utilised in a gas turbine, internal combustion engine

or direct injection diesel engine as demonstrated by researchers. The energy recovery processes seem to be technically and economically feasible with possibility of integration to energy system.

Corresponding Author(s)

*Sultan Majed Al-Salem (ssalem@kisr.edu.kw), A. Constantinou (constaa8@lsbu.ac.uk)

Author Biographies

Ms. A. Antelava graduated with a BEng in Chemical and Process Engineering from London South Bank University in 2017. During her BEng she was worked on thermal and catalytic pyrolysis of plastic solid waste for energy recovery. Currently, Ana is undertaking her PhD at the London South Bank University and the National Structural Research Centre working on developing durable super repellent coatings.

Ms. N. Jablonska graduated with a BEng (Hons) in Chemical and Process Engineering from the London South Bank University in 2017. Following her graduation, Natalia started working for Lagoni Engineering as a Technical Safety Engineer and was later promoted to a Functional Safety Consultant. She works mainly with safety systems at LNG terminals and HP gas transmission systems, however her interests are more oriented around alternative, sustainable sources of energy.

Dr. A. Constantinou is an Assistant Professor of Chemical Engineering with positions held at UCL, LSBU and CUT. He specialises in chemical and catalytic reaction engineering and in particular, the design of multiphase reactors to intensify and improve their performance. Dr. Constantinou holds the titles of Chartered Chemical Engineer (MIChemE), Chartered Engineer (CEng) and Chartered Scientist (CSci). Dr. Constantinou has contributed to a number of book chapters, peer-reviewed journal and conference articles.

Dr. Manos is an Associate Professor at the Chemical Engineering Department of University College London. His research involves hydrocarbon reaction process chemistry with a focus on polymer catalytic pyrolysis and catalyst deactivation by coking. He is also working on statistical mechanical modelling of adsorption in zeolites and MOFs. Dr. Manos is the author of a number of refereed journal papers, book chapters and conference papers.

Dr. S. Salaudeen is mechanical engineering graduate with a strong background in Thermofluid systems applicable to process engineering, energy modelling and analysis, clean and renewable

energy, CO_2 capture, power generation, gas production, thermochemical conversion, combustion and emissions, and heating, ventilation and air conditioning. His research interests expand in the following areas: Biomass Conversion, Gasification, Carbon Capture, Renewable Energy, Combustion and Emissions. Currently he is a research fellow at the University of Guelph.

Prof. A. Dutta's research focuses on energy, primarily clean and sustainable-renewable technologies. Since his tenure with the school of engineering, he has been taking initiative in developing a biomass conversion research program (BCRP) by securing research funding from a number of governmental agencies and industry. The broad objective of his research program is to help Canada better meet the challenges of climate change and environmental degradation through advanced biomass conversion technologies and CO_2 sequestration.

Dr. S.M. Al-Salem currently holds the position of a Research Scientist at the Environment & Life Sciences Research Centre of KISR working on a number of research projects and pursuing a number of major R&D works. He is also the Environmental Pollution & Climate Program (EPCP) manager as of 2019. He specializes in polymer degradation kinetics, polymer weathering, plastic solid waste management, reactor design, waste to energy technologies and life cycle assessment.

Author Contributions

A.A. Initial Draft Preparation and Data Analysis/Critical Review, N.J. Initial Draft Preparation and Data Analysis/Critical Review, A.C. Data Analysis, Initial and Final Draft Preparation/Review, G.M. Final Draft Preparation/Review, S.A.S. Initial Draft Preparation and Data Analysis/Critical Review, A.D. Data Analysis, Initial and Final Draft Preparation/Review, S.M.A. Conceptualization, Data Analysis, Initial and Final Draft Preparation/Review.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this work.

ABBREVIATIONS

CE Circular Economy, CCE Carbon Conversion Efficiency; CGE Cold Gas Efficiency; CO_2 Carbon Dioxide; CV Calorific Value; ER Equivalence Ratio; FBP Final Boiling Point; HC Hydrocarbons; HCV Higher Calorific Value; HDPE High Density Polyethylene; HIPS High Impact Polystyrene; LDPE Low Density Polyethylene; MSW Municipal Solid Waste; MPW Mixed Plastic Waste; N_2 Nitrogen; NO_x Nitrogen Oxides; PE Polyethylene; PET Polyethylene Terephthalate; PP Polypropylene; PP&A Polyphthalamide; PS Polystyrene; PUR Polyurethane; PVC Polyvinyl Chloride; PW Plastic Waste; RP Recycled Plastic; SCW Supercritical Water; SO_x Sulphur Oxides; TCC Thermochemical Conversion; WRPC Virgin Wood and Coal; WtE Waste to Energy

References

[1] Geyer, R., Jambeck, J. R., Law, K. L., 2017. Production, use, and fate of all plastics ever made. Science Advances, 3(7), p.e1700782.

[2] Curbellplastics.com. 2021. Curbell Plastics Website. [online] Available at: https://www.curbellplastics.com/Research-Solutions/Plastic-Properties [Accessed 14th January 2021].

[3] Al-Salem S. M., Lettieri P., Baeyens J., 2009. Recycling and recovery routes of plastic solid waste (PSW): A review. Waste Management, 29(10): 2625-2643

[4] Hopewell J., Dvorak R., Kosior E., 2009. Plastics recycling: challenges and opportunities. Philos. Trans. R. Soc. B Biol. Sci., 364, 2115-2126.

[5] Hafeez, Sanaa et al. "Liquid Fuel Synthesis In Microreactors". Reaction Chemistry & Engineering, vol 3, no. 4, 2018, pp. 414-432. Royal Society Of Chemistry (RSC), doi:10.1039/c8re00040a. Accessed 12 Jan 2021.

[6] Singh, R., Ruj, B., Sadhukhan, A. and Gupta, P., 2019a. Thermal degradation of waste plastics under non-sweeping atmosphere: Part 1: Effect of temperature, product optimization, and degradation mechanism. Journal of Environmental Management, 239, pp.395-406.

[7] PE, 2018. Plastics: The Facts 2018. An Analysis Of European Plastics Production, Demand And Waste Data., 2018 [online] Available at: https://www.plasticseurope.org/application/files/6315/4510/9658/Plastics_the_facts_2018_AF_web.pdf

[8] UN, 2017. United Nations World Population Prospects: The 2017 Revision, Key Findings and Advance Tables. New York (2017).

[9] Kedzierski M., Frère D., Le Maguer G., Bruzaud S., 2020. Why is there plastic packaging in the natural environment? Understanding the roots of our individual plastic waste management behaviours. Science of The Total Environment 740, 139985.

[10] Geyer R., Jambeck J.R., Law K.L., 2017. Production, use, and fate of all plastics ever made. Sci. Adv., 3 (2017), Article e1700782.

[11] Khan, I. and Kabir, Z., 2020. Waste-to-energy generation technologies and the developing economies: A multi-criteria analysis for sustainability assessment. Renewable Energy, 150, pp.320-333.

[12] Ilyas, M., Ahmad, W., Khan, H., Yousaf, S., Khan, K. and Nazir, S., 2018. Plastic waste as a significant threat to environment – a systematic literature review. Reviews on Environmental Health, 33(4), pp.383-406.

[13] Al-Salem S.M., A. Antelava, A. Constantinou, G. Manos, A. Dutta, 2017. A review on thermal and catalytic pyrolysis of plastic solid waste (PSW). Journal of Environmental Management, 197: 177-198.

[14] Singh, R., Ruj, B., Sadhukhan, A. and Gupta, P., 2019b. Impact of fast and slow pyrolysis on the degradation of mixed plastic waste: Product yield analysis and their characterization. Journal of the Energy Institute, 92(6), pp.1647-1657.

[15] US Energy Information Administration. International Energy Outlook 2019. http://www.eia.gov/ieo [accessed May 12, 2020].

[16] Singh, P., Déparrois, N., Burra, K., Bhattacharya, S. and Gupta, A., 2019c. Energy recovery from cross-linked polyethylene wastes using pyrolysis and CO2 assisted gasification. Applied Energy, 254, p.113722.

[17]   Alli, R. D., Kannan, P., Al Shoaibi, A. and Srinivasakannan, C., 2018. Performance prediction of waste polyethylene gasification using CO2 in a bubbling fluidized bed: A modelling study. Chemical and Biomedical Engineering Quarterly 32(2), pp. 349-358.

[18]   Fox, J. and Stacey, N., 2019. Process targeting: An energy based comparison of waste plastic processing technologies. Energy, 170, pp.273-283.

[19]   Chua, H., Bashir, M., Tan, K. and Chua, H., 2019. A sustainable pyrolysis technology for the treatment of municipal solid waste in Malaysia. 6TH INTERNATIONAL CONFERENCE ON ENVIRONMENT (ICENV2018): Empowering Environment and Sustainable Engineering Nexus Through Green Technology.

[20]   Bai, B., Liu, Y., Wang, Q., Zou, J., Zhang, H., Jin, H., Li, X., 2019. Experimental investigation on gasification characteristics of plastic wastes in supercritical water. Renewable Energy, 135, pp. 32-40

[21]Al-Salem, S.M., Zeitoun, R., Dutta, A. et al. 2020. Baseline soil characterisation of active landfill sites for future restoration and development in the state of Kuwait. Int. J. Environ. Sci. Technol.

[22]   Perugini, F., Mastellone, M. and Arena, U., 2005. A life cycle assessment of mechanical and feedstock recycling options for management of plastic packaging wastes. Environmental Progress, 24(2), pp.137-154.

[23]   Gaurh, Pramendra, and Hiralal Pramanik., 2018. A Novel Approach Of Solid Waste Management Via Aromatization Using Multiphase Catalytic Pyrolysis Of Waste Polyethylene". Waste Management, vol 71, pp. 86-96. Elsevier BV, doi:10.1016/j.wasman.2017.10.053.

[24]   Wong, S., Ngadi, N., Abdullah, T. and Inuwa, I., 2015. Current state and future prospects of plastic waste as source of fuel: A review. Renewable and Sustainable Energy Reviews, 50, pp.1167-1180.

[25]   Patni, N., Shah, P., Agarwal, S. and Singhal, P., 2013. Alternative strategies for conversion of waste plastic to fuels. ISRN Renewable Energy, pp. 1-7.

[26]   Lopez, G., Artetxe, M., Amutio, M., Alvarez, J., Bilbao, J., Olazar, M., 2018. Recent advances in the gasification of waste plastics. A critical overview. Renewable and Sustainable Energy Reviews, 82, pp. 576-596

[27]   Arena, U., 2012, Process and technological aspects of municipal solid waste gasification. A review. Waste Management, 32, pp. 625-639

[28]   De Filippis, P., Scarsella, M., Verdone, N., Carnevale G. B., 2015. Batch waste gasification technology: characteristics and perspectives. WIT Transactions on State of the Art in Science and Engineering, Vol 84. Waste to Energy, pp. 125-132.

[29]   Chen, D., Yin, L., Wang, H. and He, P., 2014. Pyrolysis technologies for municipal solid waste: A review. Waste Management, 34, 2466–2486

[30]   Syamsiro, M., Saptoadi, H., Norsujianto, T., Noviasri, Cheng, S., Alimuddin, Z. and Yoshikawa, K., 2014. Fuel oil production from Municipal plastic wastes in sequential pyrolysis and catalytic reforming reactors. Energy Procedia, 47, 180–188

[31]   Fogler, H. 2016. Elements Of Chemical Reaction Engineering. Pearson Education. ISBN 978-0-13-388751-8

[32]   Anuar Sharuddin, S., Abnisa, F., Wan Daud, W. and Aroua, M., 2016. A review on pyrolysis of plastic wastes. Energy Conversion and Management, 115, pp.308-326.

[33]   Al-Salem S.M., 2019. Thermal pyrolysis of high density polyethylene (HDPE) in a novel fixed bed reactor system for the production of high value gasoline range hydrocarbons (HC). Process Safety and Environmental Protection, 127, 171-179.

[34]   López, G., Olazar, M., Aguado, R. and Bilbao, J., 2010. Continuous pyrolysis of waste tyres in a conical spouted bed reactor. Fuel, 89(8), pp.1946-1952.

[35]   Faussone, G., 2018. Transportation fuel from plastic: Two cases of study. Waste Management, 73, pp.416-423.

[36]   Miandad, R., Barakat, M. A., Aburiazaiza, A. S., Rehan, M., Ismail, I. M. I. and Nizami, A. S, 2017. Effect of plastic waste types on pyrolysis liquid oil. International Biodeterioration & Biodegradation, 119, pp.239-252.

[37]   Papuga, S., Gvero, P. and Vukic, L., 2016. Temperature and time influence on the waste plastics pyrolysis in the fixed bed reactor. Thermal Science, 20(2), pp.731-741.

[38]   Zhang, Yutao et al. 2020. Exergy And Energy Analysis Of Pyrolysis Of Plastic Wastes In Rotary Kiln With Heat Carrier. Process Safety And Environmental Protection, vol 142, pp. 203-211. Elsevier BV, doi:10.1016/j.psep.2020.06.021.

[39]   Demirbas A., 2005. Recovery of chemicals and gasoline-range fuels from plastic wastes via pyrolysis. Energy Sources, 27, pp. 1313-1319.

[40]   Jiang, G., Wang, J., Al-Salem, S. M. and Leeke, G. A., 2020. Molten solar salt pyrolysis of mixed plastic waste: Process simulation and technoeconomic evaluation. Energy & fuels, 34, pp. 7397-7409.

[41]   Quesada, L. et al. "Characterization Of Fuel Produced By Pyrolysis Of Plastic Film Obtained Of Municipal Solid Waste". Energy, vol 186, 2019, p. 115874. Elsevier BV, doi:10.1016/j.energy.2019.115874. Accessed 9 Jan 2021.

[42]   Sharma, B., Moser, B., Vermillion, K., Doll, K. and Rajagopalan, N., 2014. Production, characterization and fuel properties of alternative diesel fuel from pyrolysis of waste plastic grocery bags. Fuel Processing Technology, 122, pp.79-90.

[43]   Miskolczi, N. et al. , 2016. Thermal Degradation Of Polyethylene And Polystyrene From The Packaging Industry Over Different Catalysts Into Fuel-Like Feed Stocks. Polymer Degradation And Stability, vol 91, no. 3, pp. 517-526. Elsevier BV, doi:10.1016/j.polymdegradstab.2005.01.056.

[44]Williams, Paul T., and Edward Slaney. 2007 "Analysis of Products From The Pyrolysis And Liquefaction Of Single Plastics And Waste Plastic Mixtures". Resources, Conservation and Recycling, vol 51, no. 4, pp. 754-769. Elsevier BV, doi:10.1016/j.resconrec.2006.12.002.

[45]   Saptoadi, H. and Pratama, N. N., 2015. Utilization of plastics waste oil as partial substitute for kerosene in pressurized cookstoves. International Journal of Environmental Science and Development, vol.6, No. 5, pp. 363-368.

[46]   Klavins, M., Bisters, V., Burlakovs, J., 2018. Small Scale Gasification Application and Perspectives in Circular Economy. Environmental and Climate Technologies, 22, pp. 42-54

[47]   Bai, B., Wang, W., Jin, H., 2020. Experimental study on gasification performance of polypropylene (PP) plastics in supercritical water. Energy, 191, 116527

[48]   Bungay, V. C., 2017, Kinetic Study on the Pyrolysis and Gasification of Plastic Waste. Chemical Engineering Transactions, Vol. 56

[49]   Clifford, C. B., 2018, 4.3 Gasification. Available from: https://www.e-education.psu.edu/egee439/node/607 [accessed 22nd January 2021].

[50]   Salaudeen, S. A., Arku, P., Dutta, A., 2019, Gasification of Plastic Solid Waste and Competitive Technologies. Plastics to Energy, Fuels, Chemicals, and Sustainability Implications. Plastic Design Library, pp. 269-293

[51]   Chen, G., Jamro, I. A., Samo, S. R., Wenga, T., Baloch, H. A., Yan, B., Ma, W., 2020. Hydrogen-rich syngas production from municipal solid waste gasification through the application of central composite design: An optimization study. https://doi.org/10.1016/j.ijhydene.2020.09.118.

[52]   Alvarez, J., Kumagai, S., Wu, C., Yoshioka, T., Bilbao, J., Olazar, M. and Williams, P.T., 2014. Hydrogen production from biomass and plastic mixtures by pyrolysis-gasification. International Journal of Hydrogen Energy, 39, pp. 10883-10891.

[53]   Pinto, F., Franco, C., Andre, R. N., Miranda, M., Gulyurtlu, I. and Cabrita, I., 2002. Co-gasification study of biomass mixed with plastic wastes. Fuel, 81, pp. 291 – 297.

[54]   Wu, C., Williams, P.T. 2010. Pyrolysis-gasification of plastics, mixed plastics and real-world plastic waste with and without Ni-Mg-Al catalyst, Fuel, vol. 89, no. 10, pp. 3022–3032.

[55]   Zaccariello, L., Mastellone, M. L., 2015, Fluidized-Bed Gasification of Plastic Waste, Wood, and Their Blends with Coal. Energies, 8, pp. 8052-8068.

[56]   Erkiaga, A., Lopez, G., Amutio, M., Bilbao, J. and Olazar, M., 2013. Syngas from steam gasification of polyethylene in a conical spouted bed reactor. Fuel, vol. 109, pp. 461–469.

[57]   Wu, C., Wang, Z., Wang, L., Williams, P. and Huang, J., 2012. Sustainable processing of waste plastics to produce high yield hydrogen-rich synthesis gas and high quality carbon nanotubes. RSC Advances, 2(10), p.4045.

[58]   Janajreh, I., Adeyemi, I., Elagroudy, S., 2020, Gasification feasibility of polyethylene, polypropylene, polystyrene waste and their mixture: Experimental studies and modelling. Sustainable Energy Technologies and Assessments, 38, 100684

[59]   Saebea, D., Ruengrit, P., Arpornwichanop, A. and Patcharavorachot, Y., 2020. Gasification of plastic waste for synthesis gas production. Energy Reports, 6, pp. 202-207.

[60]   Radenahmad, N., Rahman, I. S. A., Morni, N. A. H., Azad, A. K., 2018, Acacia-Polyethylene Terephthalate Co-Gasification as Renewable Energy Resource. International Journal of Renewable Energy Research, vol 8, no. 3

[61]   Arena, U., Zaccariello, L. and Mastellone, M. L., 2009. Tar removal during the fluidized bed gasification of plastic waste. Waste Management, 29, pp. 783-791.

[62]   Kannan, P., Al Shoaibi, A. and Srinivasakannan, C., 2013. Energy recovery from co-gasification of waste polyethylene and polyethylene terephthalate blends. Computers & Fluids, vol. 88, pp. 38–42.

[63]   Xiao, R., Jin, B., Zhou, H., Zhong, Z. and Zhang, M., 2007. Air gasification of polypropylene plastic waste in fluidized bed gasifier. Energy Conversion and Management, vol. 48, no. 3, pp. 778–786.

[64]   Qureshi, M., Oasmaa, A., Pihkola, H., Deviatkin, I., Tenhunen, A., Mannila, J., Minkkinen, H., Pohjakallio, M. and Laine-Ylijoki, J., 2020. Pyrolysis of plastic waste: Opportunities and challenges. Journal of Analytical and Applied Pyrolysis, p.104804.

[65]   Ghenai, C., Alamara, K. and Inayat, A., 2019. Solar Assisted Pyrolysis of Plastic Waste: Pyrolysis oil Characterization and Grid-Tied Solar PV Power System Design. Energy Procedia, 159, pp.123-129.

[66]   Mastellone, M., 2019. A feasibility assessment of an integrated plastic waste system adopting mechanical and thermochemical conversion processes. Resources, Conservation & Recycling: X, 4, p.100017.

[67]   Dong, J., Tang, Y., Nzihou, A., Chi, Y., Weiss-Hortala, E. and Ni, M., 2018. Life cycle assessment of pyrolysis, gasification and incineration waste-to-energy technologies: Theoretical analysis and case study of commercial plants. Science of The Total Environment, 626, pp.744-753.

[68]   Gutiérrez Ortiz, F., Kruse, A., Ramos, F. and Ollero, P., 2019. Integral energy valorization of municipal solid waste reject fraction to biofuels. Energy Conversion and Management, 180, pp.1167-1184.

[69]   Kalargaris, I., Tian, G. and Gu, S., 2017. Combustion, performance and emission analysis of a DI diesel engine using plastic pyrolysis oil. Fuel Processing Technology, 157, pp.108-115.Al-Salem S.M., A. Antelava, A. Constantinou, G. Manos, A. Dutta, 2017. A review on thermal and catalytic pyrolysis of plastic solid waste (PSW). Journal of Environmental Management, 197: 177-198.

[70]   Miandad, R., Barakat, M., Aburiazaiza, A., Rehan, M. and Nizami, A., 2016. Catalytic pyrolysis of plastic waste: A review. Process Safety and Environmental Protection, 102, pp.822-838.

[71]   Phetyim, N. and Pivsa-Art, S., 2018. Prototype Co-Pyrolysis of Used Lubricant Oil and Mixed Plastic Waste to Produce a Diesel-Like Fuel. Energies, 11(11), p.2973.

[72]   BS EN 590:2013 Diesel Fuel Specification. ISBN 978 0 539 14963 0.

[73]   Laurence, L. C., and Ashenafi, D., 2012. Syngas Treatment Unit for Small Scale Gasification – Application to IC Engine Gas Quality Requirement. Journal of Applied Fluid Mechanics, Vol. 5, No. 1, pp. 95-103.

[74]   Maitlis, P. M., 2013, Other Industrially Important Syngas Reactions. Greener Fischer-Tropsch Processes for Fuels and Feedstocks, First Edition. Wiley-VCH Verlag GmbH & Co. KGaA.

[75]   Lee, J. W., Yu, T. U., Lee, J. W., Moon, J. H., Jeong, H. J., Park, S. S., Yang, W. and Lee, U. D. 2013. Gasification of mixed plastic wastes in a moving-grate gasifier and application of the producer gas to a power generation engine. Energy & fuels, 27(4), pp. 2092-2098.

[76]   Vadxx, 2016. Vadxx energy establishes waste plastic to Ecofuel™ facility in Akron. Available at: https://jsquaredohio.com/vadxx-energy-establishes-waste-plastic-to-ecofuel-facility-in-akron/ [accessed 20th August 2020].

[77]   Fukushima, M., Shioya, M., Wakai, K. and Ibe, H., 2009. Toward maximizing the recycling rate in a Sapporo waste plastics liquefaction plant. Journal of Material Cycles and Waste Management, 11(1), pp.11-18.

[78]   Brightmark, 2020. Brightmark: Indiana Advanced Recycling Plant. Available from: https://www.brightmark.com/work/ashley-plastics-renewal-facility/ [accessed 20th August 2020]

[79]   Yuan, H., Yin, H., Tang, Y., Shuai, H., 2014. The Basic Characteristics of Gasification Slag from Texaco Gasifier and Shell Gasifier. Applied Mechanics and Materials Vols. 675-677 pp 728-732.

[80]   Seifert, W., Buttker, B., 2000. Materials recycling in SVZ Schwarze Pumpe GmbH via the route of gasification, production of synthesis gas, methanol production; Stoffliche

Abfallverwertung ueber die Route Vergasung, Synthesegasherstellung, Methanolgewinnung in der SVZ Schwarze Pumpe GmbH. Germany: N. p., 2000. Web.

[81] Patt.gov.gr, 2020. Peccioli dumping ground [online] Available at: http://www.patt.gov.gr/site/attachments2/5859_Peccioli_best_practices.pdf [Accessed 21st August 2020].