Paradigm Academic Press
Innovation in Science and Technology
ISSN 2788-7030
MAR. 2023 VOL.2, NO.2

Pyrolysis in the Chemical Industry and Its Major Industrial Applications

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doi:10.56397/IST.2023.03.01

Abstract

Pyrolysis is an irreversible thermochemical treatment process of materials at elevated temperatures in an inert atmosphere.

Pyrolysis is used heavily in the chemical industry to produce many forms of carbon and other chemicals from petroleum, coal, wood, oil shale, biomass or organic waste materials, and it is the basis of several methods for producing fuel from biomass. The end products of pyrolysis include solid residual coproducts and ash, noncondensable gases and condensable liquids. These products can be controlled by optimizing pyrolysis parameters such as temperature and residence time.

Keywords: pyrolysis, torrefaction, thermal decomposition, destructive and dry distillation, charring, tyre recycling, liquefaction, carbonisation, coking, cracking

1. Introduction

Pyrolysis, or thermolysis, is an irreversible thermochemical treatment process of complex solid or fluid chemical substances at elevated temperatures in an inert or oxygen-free atmosphere. It is in essence a carbonisation process where an organic material is decomposed to produce a solid residue with high (or higher) carbon content and some volatile products. The decomposition reactions are accompanied in general with polymerisation and isomerisation reactions. Pyrolysis also is the process of conversion of buried organic matter into fossil fuels (H. Al-Haj Ibrahim, 2020).

The rate of pyrolysis is temperature-dependent, and it increases with temperature. The pyrolysis end products can also be controlled by optimizing other pyrolysis parameters such as heating rate, residence time, pressure, feed particle size and type of reactor (H. Al-Haj Ibrahim, 2020) (Table 1). Reactor types include packed or fixed-bed reactors, rotary kiln reactors and fluidized bed reactors. Fluidized bed reactors in particular, such as the auger, bubbling fluidized bed reactor and the circulating fluidized bed reactor, are highly efficient for the large commercial-scale production of pyrolysis oil (A. V. Bridgwater, 2003; A. V. Bridgwater & G.V.C. Peacocke, 2000; A. V. Bridgwater, 2004) (Table 2).

Table 1. Effect of the pyrolysis process and parameters on the yield of pyrolysis products

	Char	Oil	Gas
Lower Pyrolysis Temperatures	Yield increase	Yield increase	
Higher Pyrolysis Temperatures			Yield increase
Lower Heating rates	Yield increase	Yield increase	

Higher Heating rates			Yield increase
Short Residence Time		Yield increase	
Low Pressures or Vacuum		Yield increase	
Higher Pressures	Yield increase		Yield increase
Larger Particle Size		Yield increase	
Rapid Quenching		Yield increase	
Catalytic Pyrolysis	Yield increase		Yield increase
Radio frequency plasma pyrolysis			Yield increase
Slow Pyrolysis	Yield increase	Yield increase	
Fast Pyrolysis			Yield increase

Table 2. Use of different types of reactors in pyrolysis processes

Type of reactor	**Pyrolysis Process**	**Ref**
Fluidized bed reactor	Pyrolysis wood feedstocks and rice straw	5
	Pyrolysis of rice straw	6
	Pyrolysis of municipal solid waste	7
Dual fluidized bed reactor	Pyrolysis of municipal solid waste	8
Fluidized sand bed reactor	Pyrolysis of different biomass to obtain olefins	9
	pyrolysis of wheat straw and aspen-poplar wood	10, 11
	Pyrolysis of almond shells at low and high temperatures	12-15
	Pyrolysis of polyethylene	16
	Pyrolysis of various types of plastics and sewage sludge	17-18
	Pyrolysis of plastics	19
	Pyrolysis of Napier Grass	20
Fixed bed reactor	Pyrolysis of rice straw, sugarcane bagasse and coconut shell	21
	Pyrolysis of shale oil	22
	Pyrolysis of biomass	23
	Pyrolysis of lignins	24
Fixed-bed tubular reactor	pyrolysis of rice straw	25
Rotary bed horizontal batch reactor	pyrolysis of scrap truck tyres	26
Semibatch, laminar flow reactor	Pyrolysis of tars from cellulose and lignin	27
Electrically heated retort	Pyrolysis of municipal solid waste	28
Two-stage reactor	Pyrolysis of wood tars	29
	pyrolysis of biomass	30
Vortex reactor followed by a tubular reactor	Pyrolysis of biomass	31

2. Industrial Applications of Pyrolysis

Pyrolysis is a proven and energetically-efficient chemical technology that is used heavily in the chemical industry. There are a great many pyrolysis processes used in the production of fuels and chemicals. Such processes differ in the type of process, the use of catalysts, the substances treated and the end products. Pyrolysis processes include catalytic and non-catalytic pyrolysis, hydrous pyrolysis, vacuum pyrolysis, slow pyrolysis, torrefaction, fast pyrolysis, fluidized bed pyrolysis, flash pyrolysis, microwave-induced pyrolysis, plasma pyrolysis, empty tube pyrolysis, on-line pyrolysis and ultrasonic spray pyrolysis (USP). Other pyrolysis processes include also thermal decomposition, destructive and dry distillation, charring, tyre recycling and pyrolysis, liquefaction, high- and low-temperature carbonisation, coking and thermal and catalytic cracking (H. Al-Haj Ibrahim, 2020).

3. End Products of Pyrolysis

The end products of pyrolysis include a wide range of materials such as charcoal, biochar, smokeless fuel, petroleum and metallurgical coke, activated carbon, carbon black, syngas, coke and coke-oven gas, shale oils, bio-oil and various cracked petroleum products. Pyrolysis is the basis of several methods for producing biofuel from biomass. A clean fuel gas with a high calorific value may be produced by the pyrolysis of many different solid hydrocarbon-based wastes.

The pyrolysis and carbonisation of solid materials such as coal and wood are normally referred to as destructive or dry distillation. Pyrolysis has been used for turning wood into charcoal since ancient times. The ancient Egyptians obtained methanol from the pyrolysis of wood, where the methanol was used in their embalming process. The dry distillation of wood remained the major source of methanol into the early 20th century. By the dry distillation of vitriol mixed with other salts, Jabir ibn Hayyan, known also as Geber, was able to discover sulphuric, hydrochloric, and nitric acids, as well as aqua regia.

During the carbonisation process of solid materials, the organic material may or may not become liquid. Organic materials that do not become liquid during carbonisation include wood and non-coking coal. The carbonisation process in this case is referred to as charring and the treated materials are transformed into chars. Chars are essentially non-graphitizable carbons. Such chars tend to be porous with pore volumes of about 1 cm^3/g, contained dominantly within microporosity. The size of stacked units of lamellae or “crystallites” is in dimensions of a few nanometers ($10^{-9}m$), these crystallites are randomly arranged. This makes such carbons isotropic when polished surfaces are viewed by polarized light optical microscopy (Figueiredo & Mouljin (ed.), 1986).

Charring is the process used for turning wood into charcoal by pyrolysis in charcoal kilns. Charring has been used since ancient times, where fires would be started and when the wood is hot enough it would be covered with earth to deprive the fire of oxygen and the high temperature would then break down the wood to produce the charcoal. The charring of wood remained the major source of methanol for a very long time. In their embalming process, the ancient Egyptians used methanol, which they obtained from the pyrolysis of wood. During the two World Wars, pyrolysis was used with wood waste feedstock to produce transportation fuel when fossil fuels were unavailable.

Lignocellulosic materials are the most abundant renewable biomass resources on earth (H. Al-Haj Ibrahim, 2018). In general, lignocellulosic (woody and herbaceous) biomass has a fibrous structure and it contains approximately 70-80% carbohydrates. It consists of three main carbon-based polymeric structures, known collectively as lignocellulose. These three natural constituents of biomass are cellulose (40-50%), hemicellulose (25-35%) and lignin (15-20%). Lignin is an aromatic and optically inactive amorphous heteropolymer. Of the three constituents of biomass, only lignin has a mole ratio of C: H: O (1: 1.3: 0.3) close to that of crude petroleum (1: 1.6: 0.05).

The type and composition of biomass determine to a large extent its behaviour in the pyrolysis process. Woody biomass is often classified as hard deciduous wood and soft coniferous wood. Although the composition and the distribution of the three lignocellulosic constituents in the two woody types are similar (Table 3), the composition of the polysugars that form the hemicelluloses fraction is very different.

Table 3. Distribution of lignocellulosic materials (wt %) in wood (R. Wagenführ & C. Scheiber, 1974)

	Deciduous wood	Coniferous wood
Cellulose	40 – 50	35 – 50
Hemicellulose	15 – 35	20 – 32
Lignin	18 – 25	25 – 35

Studies on the thermal decomposition of biomass lignocellulosic materials showed that the hemicelluloses, which are the most reactive components, decompose first, at 200-260°C, followed by the celluloses at 240-350°C and finally by the lignin at 280-500°C (M.V. Ramiah, 1970; E. Shafizadeh & W.F. DeGroot, 1976). Pyrolysis causes the cellulose, hemicellulose, and part of the lignin in the biomass to disintegrate to smaller molecules that condense to form bio-oil, while the remainder of the original mass (mainly the remaining lignin) is left as solid biochar and noncondensable gases. It has been reported that the bio-oil produced contains large molecules derived from lignin, which adversely affects its properties (J. R. Diebold, 1985; Figueiredo and Mouljin (ed.), 1986). Through kinetic analysis of the pyrolysis of rice straw, cellulose and lignin, it was found by Nakamichi et al. that kinetic parameter values of plant biomass were strongly dependent on the ratio of cellulose and lignin components (K. Nakamichi et al., 1984). In the relatively low temperature range of torrefaction, the hemicelluloses are the components that are mainly decomposed.

Pyrolysis efficiency and product quality may not always be as good as expected when raw biomass is used owing to the properties of raw biomass such as high moisture, oxygen, and alkali metal contents. In this regard, wood and straws would in general be desirable biomass materials because they are abundant and relatively clean with relatively lower moisture and ash contents. Experimental results indicate that three phases are involved in biomass pyrolysis, namely moisture evaporation, a main devolatilization phase, and final devolatilization (G. Chen et al., 2003). Biomass pyrolysis may be carried out in a fixed-bed reactor or in a bubbling fluidized bed equipped with a char separation system.

Biochar is a kind of porous charcoal. It is generally a product of the pyrolysis of biomass such as wood and sugarcane and biowaste materials. If mixed with soils, it serves as a fertilizer and used to improve soil properties and sustainable agricultural production. For the production of biochar, biomass materials may be crushed and subjected to fast heating rates in a fast pyrolysis process with the production of high-quality ethylene-rich syngas, or the biomass materials may be less finely crushed and subjected to low heating rates in a slow pyrolysis process with the resulting increase of biochar yields.

On pyrolysis of biomass, the pyrolysis oil is first produced at lower temperatures, but it can undergo later on secondary cracking and re-polymerisation reactions as the temperature is increased (D. Ferdous et al., 2001; G. Chen et al., 2003; A. E. Pütün et al., 2004). The pyrolysis oil is a complex mixture of components that can be converted to liquid fuels as well as commodity chemicals. The bio-oil components comprise various groups of organic compounds, in which acids, phenolics, furans, aldehydes and hydrocarbons are the main components (G. Qi et al., 2010). Pyrolysis oil produced by fast pyrolysis of biomass may not be regarded in general as a proper conventional hydrocarbon fuel oil. This is mainly because it is acidic in nature, polar and not miscible with crude petroleum. In addition, it is unstable, as some repolymerisation of organic matter in the oil causes an increase in viscosity in time. The high levels of oxygen-containing functional groups in the pyrolysis oil are reported to be the main cause for its unstable character. Furthermore, it has a strong tendency for coking at elevated temperatures. A number of catalytic approaches have been proposed to upgrade and improve the product properties of fast pyrolysis oil including catalytic cracking and catalytic hydro processing or hydrotreating, where fast-pyrolysis oil is treated with hydrogen in the presence of a heterogeneous catalyst (R. H. Venderbosch & H. J. Heeres, 2011).

Organic materials such as rice hulls, wood, straw, nut hulls, olive pits, coal, paper, bagasse, plastic, rubber and rags were pyrolyzed in a 2-stage process, the 1st to produce hydrocarbons and the 2nd to decompose long-chain hydrocarbons to low molecular-weight fuel gases by controlling the water gas equilibrium (H. Mallek and J.L. Gruendling, 1988).

Pyrolysis of straw and other biomass materials for the production of hydrogen-rich gas may be carried out in a two-stage reactor where the first-stage reactor is a conventional fixed-bed pyrolyzer, and the second-stage reactor is a catalytic fixed bed using an appropriate catalyst such as nickel-based catalysts. The operation of the catalytic reactor appears to be significant in promoting biomass pyrolysis towards the production of gaseous products, especially hydrogen. The catalytic bed can significantly reduce the level of tar which is carried out with the producer gas to less than 1% of its original level (G. Chen et al., 2008).

Pyrolysis of straw for the production of bio-oil may be a slow or a fast pyrolysis process (G. Qi et al., 2010; J. R. Longanbach & F. Bauer, 1975; K. Pober & H. Bauer, 1977). For the fast pyrolysis of straw, a bubbling fluidized bed with discontinuous feed may be applied. In one process, rice straw and bamboo sawdust were pyrolyzed in a bubbling fluidized bed equipped with a char removal system, where the use of the produced gas as a fluidizing medium enhanced the production of bio-oil. The char removal system is composed of a cyclone and a hot filter. High-quality bio-oils with low concentrations of alkali and alkaline earth metals were produced. The main compounds of the bio-oils were phenols, furfural, acetic acid, levoglucosan, guaiacol and alkyl guaiacol. The optimal reaction temperature for the production of bio-oil was found to be between 440 and 500ºC in the case of the rice straw and 405-450°C in the case of the bamboo sawdust. Increasing the reaction temperature tends to reduce the oil yield. A higher feed rate and a smaller feed size were found to be more effective in the production of bio-oil (S. Jung et al., 2008; B. Kang et al., 2006). The calorific value of the bio-oil produced from corn straw was 16-18 MJ/kg (G. Qi et al., 2010). The quality and practical application of bio-oil as fuel is closely dependent on its viscosity, where high viscosity fuel results in general in poor atomization and incomplete combustion, formation of excessive carbon deposits on the injection nozzles and the combustion chamber, and contamination of the lubricating oil with unburnt residues. One advantage of the bio-oil produced from rice straw is its low viscosity due to its high-water content. Bio-oil produced from rice straw has a minimum kinetic viscosity of about 5–10 mPa.s (Z. Luo et al., 2004; C. Karunanithy & K. Muthukumarappan, 2011).

Rice straw is one of the most abundant renewable resources. It is composed of cellulose (32-55%), hemicellulose (29-37%) and lignin (5-17%) (J. Peng et al., 2008; T. Raj et al., 2015). Rice straw has several characteristics that make it an attractive lignocellulosic material for bioethanol production, such as high cellulose and hemicelluloses content that can be readily hydrolyzed into fermentable sugars. The high ash and silica content of rice straw, however, makes the selection of an appropriate pre-treatment technique a major challenge in developing an economically-viable technology for bioethanol production (H. Al-Haj Ibrahim, 2012).

Rice straw may be carbonised to produce a fuel gas and a carbonised semi-coke product which is processed into charcoal briquettes by the addition of a water-soluble polymer binder by mechanical pressing (H. Al-Haj Ibrahim, 2018; Y. F. Huang et al., 2010). The pyrolysis mechanism of rice straw was investigated by Fu et al. using a tube reactor with Fourier transform IR spectroscopy and thermogravimetric analyzer. The results show that the maximum pyrolysis rate increases with increasing heating rate and temperature. The pyrolysis mechanism of rice straw at low temperatures was found to be quite different from that at high temperatures (K. Nakamichi et al., 1984). The main pyrolysis gas products include H_2O, CO_2, CO, CH_4, HCHO (formaldehyde), HCOOH (formic acid), CH_3OH (methanol) and C_6H_5OH (phenol), with maximum release of H_2O, CO_2, CO and CH_4 at 220-400ºC. At about 350ºC aromatization starts and continues to increase at higher temperatures while the amounts of ether groups decrease (P. Fu et al., 2009).

Fast pyrolysis with a high heating rate tends to increase the cavities in the biochar produced from rice straw.

Slow pyrolysis of rice straw was performed in a fixed-bed tubular reactor under nitrogen atmosphere at a heating rate of 5ºC/min, and different pyrolysis temperatures. The maximum oil yield was attained at a pyrolysis temperature of 550ºC (B. B. Uzun et al., 2004). Similar results were also obtained by Putun et al. who investigated the effects of other factors and achieved maximum yield for particle size of $0.425 < Dp < 0.85$ mm and nitrogen flow rate of 200 ml/min. (A. E. Pütün et al., 2004).

Torrefaction of straw with pelletisation is gaining attention, because it increases its energy density, making it possible to transport it still further. This processing step also makes storage much easier, because torrefied straw pellets are hydrophobic. Because the torrefied straw pellets have superior structural, chemical and combustion properties to coal, they can replace all coal and turn a coal plant into an entirely biomass-fed power station.

Radio frequency plasma technology was used for the pyrolysis of rice straw at temperatures of 740, 813, 843 and 880 K; the corresponding yields of gas products (excluding nitrogen) were 30.7, 56.6, 62.5 and 66.5 wt.% with respect to the original dried sample (W. Tu et al., 2009).

Low-temperature pyrolysis was found to be the most promising process for the production of powdered fuels from cellulose and municipal solid wastes.

Scrap vehicle tyres are a huge problem throughout the world. In 2016, it was estimated that over 1.5 billion scrap tyres are discarded annually, weighing about 17 million tons (S. Ouyang et al., 2018). Vehicle tyres are generally made up of more than a hundred different materials. These include rubber (38%), fillers (30%), reinforcing materials (16%), plasticizers and chemicals (16%). The inclusion of the reinforcing materials (steel, rayon and nylon), and the process of vulcanisation, make tyres particularly difficult to recycle. Treatment methods for the recovery of energy and chemicals from waste tyres include pyrolysis, incineration, co-combustion, liquefaction and gasification. Pyrolysis, however, remains the preferred method of treatment because of its simplicity, adaptability and lower air emissions.

A number of pyrolysis processes have been developed for the treatment of scrap tyres including vacuum pyrolysis, molten salt pyrolysis, flash pyrolysis, slow pyrolysis in a batch reactor and steam cracking. Vacuum pyrolysis of tyres has been used in Canada for the production of high-value chemicals, such as limonene (M. Bajus & N. Olahová, 2011; Y. Yongrong et al., 2000). Prior to 2000, more than 30 pyrolysis processes have been patented in China alone (Y. Yongrong et al., 2000).

In scrap tyre pyrolysis, tyres are broken down in an atmosphere of nitrogen or in the presence of steam into products which can be grouped into two types:

(1) Primary products (solid char, liquid and gas). The pyrolysis oil is a complex mixture of organic compounds of 5-20 carbon with a higher proportion of aromatics. The pyrolysis oil may, however, have high sulphur content and should therefore be desulphurised.

(2) Secondary products (oil usable for fuel such as biodiesel, and carbon black usable as filler or as activated carbon in filters and fuel cells).

The yields and properties of the tyre pyrolysis products depend on a number of parameters, including pyrolysis temperature, efficiency of heat transfer to and within the tyre mass, residence time, the type and characteristics of the feed stock including feed particle size and the specific characteristics of the pyrolysis system used such as size and type of reactor. For total decomposition and complete pyrolysis of scrap tyres, a temperature greater than 475°C is generally required. At temperatures greater than 475°C, the gas yield continues to increase while the char yield remains almost constant. The liquid yield, on the other hand, starts to decrease above 475°C to reach a minimum value at 575°C. This is probably due to secondary carbonisation reactions of oil hydrocarbons into permanent gases and char.

Increasing the feed particle size leads to increased char yield and decreased liquid and gas yields. In larger feed particle size, the heating rate is low due to its low thermal conductivity and heat can flow only to a certain depth in the available pyrolysis time compared to almost complete thermal decomposition of the smaller pieces. Thus, the rubber core of the larger pieces becomes carbonised and cannot be decomposed completely resulting in increased char yields and decreased liquid and gas yields.

Increasing the residence time leads to secondary pyrolysis reactions and hence increases slightly the gas yield and reduces the char and liquid yields.

In a study by Prathmesh and Paresh (M. Bhatt Prathmesh & D. Patel Paresh, 2012), pyrolysis of scrap truck tyres was carried out in a rotary bed horizontal batch reactor at a temperature of 430°C. The pyrolysis oil produced was found to have properties similar to the properties of diesel fuel in terms of its calorific value and carbon and hydrogen contents but with higher viscosity. Comparison of the performance characteristics of diesel fuel and different blends of tyre pyrolysis oil and diesel fuel in a four-stroke single-cylinder diesel engine was investigated by Younus et al. (S. M. Younus et al., 2013). It was found that the brake thermal efficiency increased with all blends when compared to the conventional diesel fuel, fuel consumption decreased and there was a significant decrease of CO, CO_2 and HC emissions (S. M. Younus et al., 2013).

In order to improve tar recovery, co-pyrolysis of tyres was carried out with other materials including coal, coal tar, pine nut shells and pistachio seeds (Y. Sun & J. Cheng, 2002). Pre-treatment of scrap tyres by immersion in waste coal tar prior to pyrolysis was found to improve the pyrolysis efficiency and the quality of the produced tar which contained more light fractions. Other pre-treatment methods include soaking of scrap tyres in organic solvents which will cause scrap tyres to swell and reduce their tensile strength (S. Ouyang et al., 2018).

Slow pyrolysis experiments at 1–10 °C/min. heating rates were conducted by Yacob et al. on human feces and the char and gas yields were quantified. Useful technical information was provided that can guide the design of a pyrolysis system to treat fecal waste, although social acceptance and scale-up issues need to be addressed through further research. Pyrolysis of human feces renders the waste free of pathogens and is a potential method of treating fecal sludge waste collected from non-sewered systems (T.W. Yacob et al., 2018).

Shale oil is produced by the pyrolysis of oil shale, which is a fine-grained bituminous sedimentary rock of low permeability which contains organic substances or kerogens. As a result of pyrolysis, the various chemical bonds of the kerogen macromolecules of the rock are decomposed and small molecules of liquid and gaseous hydrocarbons as well as nitrogen, sulphur and oxygen compounds are liberated. In general, shale oil production is increased using higher heating rates in a fast pyrolysis process.

Cokes are graphitizable carbons made from fusible organic materials such as coking coals, petroleum pitches and residues, aromatic oils and some model organic compounds. At least part of these organic materials passes through a liquid or a liquid crystalline state during carbonisation, where nematic liquid crystals or mesophase are homogeneously precipitated from the liquid state ultimately replacing the parent fluid pitch. The carbonisation of coal may be carried out at high temperatures in high-temperature carbonisation, or coking, with the production of high-temperature coke; or it may be carried out at low temperatures (500-750°C) in low-temperature carbonisation with the production of low-temperature coke. Metallurgical coke is made from bituminous coal which is heated at very high temperatures in coke ovens. Carbonisation and coking of coal were first developed by Simon Sturtevant in 1612.

Coke of high calorific value and low ash content may also be manufactured from municipal and industrial wastes and farmyard manure by a carbonisation process.

Petroleum coke, or petcoke for short, is made from petroleum pitches and residues by one of several carbonisation processes known as coking processes. In coking or coke making, petroleum residuum is heated to very high temperatures to produce some volatile products and a solid petroleum coke. Coking processes that can be employed for making petcoke include contact coking, fluid coking, flexicoking and delayed coking. In fluid coking fluid coke is produced in a continuous fluidized bed process by spraying the heated residuum into a fluidized bed of hot coke particles. Delayed petcoke is produced by the delayed coking process, which is a semi-continuous batch process carried out in two coke drums.

In the petroleum refining industry, heavy petroleum fractions are treated by heating in an oxygen-free atmosphere to elevated temperatures at high pressure. This process is known as thermal cracking or catalytic cracking, if a catalyst is used in the process. The Burton Pressure Distillation Process is the oldest thermal cracking process which was a liquid-phase cracking process. Several thermal cracking processes were later developed including what was known as Tube and Tank Processes where gas oil was treated at high temperatures and pressures. Thermal cracking processes are still used today mainly for the production of gas oil and coke from petroleum residua and in the petrochemical industry for the production of petrochemicals from naphtha or paraffin wax. Thermal cracking is also the basis of the reforming processes used to improve the octane number of gasoline. In most cases, however, thermal cracking has been superseded by catalytic cracking processes, and particularly the fluidized-bed catalytic cracking (FCC) process which is used in about 80% of all cracking plants. Cracking products include cracked or pressure distillate, cracked distillate fuels and residua (tar).

A wide range of products, including alkanes, alkenes and aromatic compounds, may be produced by the catalytic cracking of unsaturated fatty acids such as oleic acid. Such results contribute to the realization of using lipid feedstocks for the production of transportation fuels (T.J. Benson et al., 2008).

Pyrolysis of plant oils gives in general products that are chemically similar to petroleum derived diesel fuel, although some of the properties of these compounds may not be acceptable such as pour point, carbon residue and ash contents. In addition, the removal of oxygen during thermal processing eliminates the environmental benefits of using an oxygenated fuel (F. Ma & M. A. Hanna, 1999; H. Fukuda et al., 2001).

The pyrolysis of triglycerides with the aim of obtaining products suitable for diesel engines was investigated by a number of workers. Thermal decomposition of triglycerides produces compounds of several classes including alkanes, alkenes, alkadienes, aromatics and carboxylic acids. The nature and relative amounts of such compounds depend largely on the type of vegetable oil used, as different vegetable oils give on pyrolysis widely different compounds. Pyrolysis of soybean oil for instance gives a lower viscosity and higher cetane number oil containing 79% carbon and 12% hydrogen (H. Fukuda et al., 2001; A. W. Schwab et al., 1988).

Pyrolysis systems may be used to treat plastic waste and a variety of organic contaminants that chemically decompose when heated. Plastics are typically organic polymers of high molecular weight. Domestic and industrial applications of plastics are continually increasing. Plastics, on the other hand, are non-biodegradable materials and the natural disposal of waste plastics would take hundreds of years. Recent concern over the proliferation of waste plastics in the environment is leading companies and research organisations to study the possibility of recycling plastics as liquid feedstock or fuel. Most recycling technologies are still in the pilot plant stage but the results are encouraging. Austria's national oil company, OMV, uses thermal cracking at temperatures of about 400°C in the presence of a hot liquid solvent to return waste plastics to crude oil. The resulting synthetic product is a sulphur-free, very light crude that can be processed with other oil in a refinery. Other technology, also based on thermal cracking, is calibrated to produce naphtha, a chemical and gasoline feedstock, or a middle distillate suitable for use as diesel, if blended with typical refinery diesel fuel. Pyrolysis oil from the pyrolysis of low-density polyethylene at a temperature range of 300-350°C was found to have properties similar to diesel fuel with lower carbon residue (S.B. Desai & C. K. Galage, 2015).

Pyrolysis of waste plastics may also be used to reduce the volume of the wastes and regenerate the monomers (precursors) to the polymers that are treated. In one study, a low heating rate (5°C/min) was used to pyrolyze waste polyethylene and polystyrene, which were heated to a temperature of 600°C. In this study, polystyrene yielded higher liquid and polyethylene yielded higher gaseous products. The weight percentage of mono-aromatics was about 63% of the total oil products. The dominant product of polystyrene was styrene, with 37%, followed by toluene, naphthalene and xylene. For polyethylene, on the other hand, the dominant product was prophenyl benzene followed by butenyl benzene (N. Kiran et al., 2000).

Co-pyrolysis of waste printed circuit boards and some compound additives (Fe_3O_4 and Si-Al zeolite) was investigated by Ziwei Ye et al. (Ziwei Ye et al., 2018). The pyrolysis oil produced has a calorific value of 33 MJ/kg and improved combustion properties.

4. Other Applications of Pyrolysis

Pyrolysis has been used for pretreatment of lignocellulosic materials for thermal conversion of cellulose and hemicellulose into fermentable sugars (E. Tomas-Pejo et al., 2008). When the materials are treated at temperatures greater than 300°C, cellulose rapidly decomposes to produce gaseous products and residual char (F.J. Kilzer & A. Broido, 1965; F. Shafizadeh & A.G.W. Bradbury, 1979). The decomposition is much slower and less volatile products are formed at lower temperatures. When zinc chloride or sodium carbonate is added as a catalyst, the decomposition of pure cellulose can occur at a lower temperature (Y. Sun & J. Cheng, 2002; F. Shafizadeh & Y.-Z Lai, 1975). Pyrolysis pretreatment prior to enzymatic hydrolysis of three waste cellulosic materials (office paper, newspaper and cardboard) was examined by Leustean where the conversion of cellulose to glucose yield from enzymatic hydrolysis was markedly improved (I. Leustean, 2009).

Torrefaction of wood and other biomass materials may be used as a pretreatment technology prior to gasification.

Torrefaction increases the relatively low energy density and the carbon content of the biomass and lowers its moisture content.

Torrefaction temperature is one of the most important parameters in torrefaction pretreatment process (Y. Uemura et al., 2011). To achieve good physical properties with a relatively high energy yield, lower temperatures and shorter residence times are applied. When treated at these conditions, softwood mixture has the highest energy (95%), followed by hardwood mixture (80%), then willow (79%), and finally eucalyptus (75%) (R.H.H. Ibrahim et al., 2013).

Other advantages of the torrefaction pretreatment process include lowering the O/C ratio of the treated material and improving its hydrophobicity, homogeneity, and grindability properties. Satpathy et al. found that the torrefied wheat and barley straw are more hydrophobic, and the moisture uptake is reduced by 61–68% under suitable torrefaction conditions (S. K. Satpathy et al., 2014).

A pre-treatment process to remove potassium and chlorine from straws may be based on pyrolysis followed by char leaching (Ayhan Demirbas, 2003; P. A. Jensen et al., 2001). The straw is pyrolysed at moderate temperatures at which the potassium is retained in the char. Potassium and residual chlorine are then extracted from the residual char by water. To evaluate this pretreatment process, wheat straw chars were experimentally investigated in the laboratory. The laboratory experiments showed that three fractions of potassium in the straw reacted differently: 35–58% of the char potassium was dissolved very fast, followed by a secondary slow potassium release that was strongly influenced by particle sizes, water temperature, char type and water KCl content. The residual 5–10% of the char potassium remains in the char and could not be removed with pure water.

Radiation pretreatment of agricultural cellulosic wastes may accelerate the subsequent enzymic hydrolysis of rice straw and rice hull by cellulase. In a study by Dela Rosa et al., gamma irradiation significantly increased the acid hydrolysis of rice straw, rice hull and corn husk (A. M. Deal Rosa et al., 1983). Irradiation by an electron-beam accelerator was found to be very effective as a form of pretreatment for enzymic hydrolysis of cellulosic materials (K. Kojima et al., 1983).

Pyrolysis is used in several types of thermal cleaning systems in order to remove organic substances such as polymers, plastics and coatings from different parts or production components. The removed organic substances are converted into volatile organic compounds, hydrocarbons and carbonised gas. Synthetic hormones and other organic contaminants, for example, may be removed from sewage sludge by pyrolysis and heavy metals remaining in the sludge may be made inert thereby allowing the sludge to be used safely as fertilizer. The cleaning systems used include molten salt baths, fluidised bed systems, vacuum and burn-off ovens, also known as heat-cleaning ovens.

Green petroleum coke is normally calcined before being used in the manufacture of carbon electrodes. The calcination of coke is a high-temperature (> 1000ºC) pyrolysis treatment of green coke in which moisture and volatile matter (hydrogen, methane and tar) are removed in order to prevent cracking due to shrinkage in the subsequent baking of the electrodes. During calcination the carbonisation and aromatization processes which began in the coker are completed, dehydrogenation and dealkylation reactions continue, and large aromatic structures fuse into highly organised shapes with definite crystalline characteristics.

In Pyrolysis-gas chromatography–mass spectrometry (Pyr-GC–MS) technique, the end products of pyrolysis are separated by gas chromatography and their compositions determined by mass spectrometry and characteristic information of the structural composition of the original complex substances can thus be obtained allowing thereby identification of these substances. Such a technique can be utilised for example for the identification of microplastics in environmental samples.

5. Conclusion

Pyrolysis is used heavily in the chemical industry to produce many forms of carbon and other chemicals from petroleum, coal, wood, oil shale, biomass or organic waste materials, and it is the basis of several methods for producing fuel from biomass. The end products of pyrolysis include solid residual coproducts and ash, noncondensable gases and condensable liquids. These products can be controlled by optimizing pyrolysis parameters such as temperature and residence time.

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