Feedstock to Oil Energy Conversion Efficiency in Pyrolysis of Organic Wastes: An Up to Date Review

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Abstract

The present study provides an up to date review of previous efforts in recent years for oil and liquids production from the pyrolysis of waste tires, plastics, biomass and co-pyrolysis of mixture organic wastes. There is growing interest in pyrolysis as a technology to treat these organic wastes to produce valuable oil, char and gas products. The most common reactors used are fixed-bed (batch), screw kiln, rotary kiln, vacuum and fluidised-bed. The key influence on the product yield, and gas and oil composition, is the type of reactor used which in turn determines the temperature and feedstock to oil energy conversion efficiency (FOECE). The FOECE of processes resulting from various operating conditions under which pyrolysis of organic wastes is carried out are reviewed. In addition to reactor conditions such as temperature and heating rates, other aspects of the organic waste pyrolysis such as catalyst type and their effects on oil yields are also reviewed. Pyrolytic oil characteristics such as heating value, sulfur content and density are summarized. The review revealed that the FOECE of a pyrolysis unit and product oil characteristic depends on the type of organic wastes pyrolyzed and the operating conditions of the pyrolysis processes.

Keyword: FOECE, organic wastes pyrolysis review.

1. Introduction

The major components of urban wastes are plastic materials, variety of biomass originated refuses and different categories of tire rubber. Plastic, biomass and tires wastes presently pose difficulties when addressing their final post use destination. The main alternatives employed today are incineration and landfill deposition. However, these are far from optimal treatment options, because they can raise environmental issues, like toxic and greenhouse gas emissions, leachates, etc., besides wasting their organic content that could be otherwise valuable in several applications. On the other hand, steady depletion of fossil fuel and increased energy demand, motivated the researchers and technologists to search and develop different energy sources. Waste to energy has been a significant way to utilize the waste sustainably, simultaneously add to meet the energy demand. One of the promising ways of taking profit of the energetic and organic value of these wastes is pyrolysis. Pyrolysis have been gaining increasing attention of the researcher for the last four decadus over the world. A lot of researches already have been completed rangeing from laboratory to commercial scale.

The main options used for treating waste tires are through the use of tires as fuel in cement kilns, other energy recovery options for tires include use in power plants and co-incineration with other wastes, tires are used in material recovery options through the production of rubberised flooring in sports fields and playgrounds, paving blocks, roofing materials, etc. A significant proportion of the waste tires are used in civil engineering applications such as road and rail foundations and embankments re-treaded. There has been great interest in alternative treatment processes for waste tires, amongst which is the use of pyrolysis technology [1, 2]. Pyrolysis is the thermal degradation of the organic components of the tires, at typical pyrolysis temperatures of 500^oC to produce an oil, gas and char product in addition to the recovery of the steel. The oil may be used directly as a fuel, added to petroleum refinery stocks, upgraded using catalysts to a premium grade fuel or used as a chemical feedstock. The gases from tire pyrolysis are typically composed of C_1–C_4 hydrocarbons and hydrogen with a high calorific value, of sufficient energy content to act as fuel to provide the heat for the pyrolysis process. The solid char consists of the carbon black filler and also char produced during the pyrolysis of the rubber. It may be used as a solid fuel, as carbon black or upgraded to produce an activated carbon.

Plastics have become an indispensable ingredient of human life. They are non-biodegradable polymers of mostly containing carbon, hydrogen, and few other elements such as chlorine, nitrogen etc. Rapid growth of the world population led to increased demand of commodity plastics. Polyethylene (PE), polypropylene (PP) and

polystyrene (PS) are major plastic components of municipal solid waste (MSW). High density polyethylene is one of the largest used commodity plastics due to its vast applications in many fields. Due to its non biodegradability and low life, plastic contributes significantly to the problem of Municipal Waste Management. To avert environment pollution of plastic wastes, they must be recycled and recovered. Plastics being petrochemical origin have inherently high calorific value. Thus they can be converted back to useful energy. Many researches have been carried out to convert the waste plastics into liquid fuel by thermal and catalytic pyrolysis and this has led to establishment of a number of successful firms converting waste plastics to liquid fuels [3].

Fast pyrolysis has been proven to be an adequate process to produce a liquid product from woody materials, with suitable fuel properties (bio-oil), in contrast to the typical slow pyrolysis method of carbonization to produce char. However, some properties of this bio-oil restrict its direct use in a diesel engine, so research is still undergoing to improve these properties (bio-oil upgrading) [4].

In general, plastic waste pyrolysis allows the production of higher liquid products yields than those obtained with tires pyrolysis. Therefore, some authors [5] studied the pyrolysis of mixtures of plastics and tires wastes and observed that the use of plastic wastes favored tires pyrolysis and allowed increasing liquid yields, whilst higher contents of tires wastes favored the formation of solid compounds.

In general most urban wastes are a mixture of variety of waste components, which adds to the complexity of their treatment separately and also add additional cost in waste to energy recovery processes. It would be easier and cost effective if the waste mix would be converted into energy together.

The main product from the pyrolysis of organic waste mix is liquid. A pyrolysis unit of high liquid yield product with high energy density, engine useable, environmental frendly are the major chalanges of the present scienists. The feedstock to oil energy conversion efficiency (FOECE) is one of the performance indicators for evaluation of successful tecthniques. Feedstock-to-oil energy conversion efficiency (FOECE) is defined as the ratio of pyrolysis oil energy to the total energy of the feedstock, which is calculated using Eq. (1).

$$\text{Conversion efficiency (FOECE)}, \quad \eta = \frac{Q_O \times W_O}{Q_R \times W_R + Q_P \times W_P + Q_B \times W_B} \times 100\% \qquad \ldots \ldots \ldots (1)$$

Where Q_R, Q_P, Q_B and Q_O represent the heating values of rubber, plastics, biomass and product oil; W_R, W_P, and W_S; W_O are the mass fractions of the rubber, plastics, biomass and product oil, respectively.

In this paper, the pyrolysis of organic wastes is reviewed in terms of the range of pyrolysis reactors used. The influence of process parameters, on the yield and FOECE from the pyrolysis of different organic wastes are discussed. The various liquid products from the pyrolysis of organic wastes are discussed in terms of their respective production conditions, their composition, characteristics, and the potential applications. The research related to producing higher value products from the organic waste pyrolysis process is also reviewed.

2. Pyrolysis of different organic solid wastes

2.1. Pyrolysis of tire waste

Yuwapornpanit and Jitkarnka [6] studied with metal-loaded zeolites and found that those are potential catalysts for upgrading the quality and quantity of waste tire pyrolysis products. The effect of Cu-support interaction on tire-derived oils, petrochemicals, and sulfur removal was studied by them using three types of zeolites (HBETA, HY and HMOR) as supports at a 5 wt% Cu loading. Catalytic pyrolysis of waste tire was operated in a bench reactor, and GC×GC-TOF/MS and SIMDIST-GC instruments were used to analyze the liquid products for chemical compositions and petroleum fractions, respectively. Sulfur in the pyrolysis products was determined by using an S-analyzer, whereas the gas composition was analyzed by using a GC-FID. As a result, all Cu-promoted catalysts can reduce more sulfur content in oils than their pure zeolites; therefore, Cu was found to enhance desulfurization of oils by converting sulfur compounds into thermodynamically stable forms on Cu. Furthermore, Cu-support interaction highly affected the sulfur removal from oils. They observed that benzene and ethylbenzeneare common petrochemicals highly produced by the Cu-loaded catalysts.

Hita et al. [7] studied scrap tire pyrolysis oil (STPO) in order to remove undesired sulfur, nitrogen and unsaturated compounds while improving the properties of its different fractions (naphtha, diesel and gasoil) toward being used as a potential blend in the refinery. The studied catalysts are NiMo supported on 5 porous materials: γ-Al$_2$O$_3$ (ALM catalyst), SiO$_2$–Al$_2$O$_3$ (ASA), SBA-15 (SBA), MCM-41 (MCM) and an equilibrated FCC catalyst (FCC). The hydrotreating runs have been carried out in a fixed bed reactor at 275–375 ^{0}C and 65 bar. A preliminary catalyst screening with a model mixture of representative STPO compounds has been performed for selecting the most active catalysts: ALM, ASA and MCM catalysts ensured the 99.9% removal of sulfur. Secondly and in the hydrotreating of STPO, our results point the suitability of ASA catalyst for obtaining the highest proportion of naphtha (25 wt%) and diesel (57 wt%).

Aydın and Ilkılıc [8] investigated the pyrolysis of waste tyres, with steel and fabric removed, in a 1.15 l capacity fixed bed reactor in nitrogen over the temperature range of 400–700 ^{0}C. They found that the oil yield increased from 31 wt.% at 400 ^{0}C, increasing to 40 wt.% at 500 ^{0}C, with little change in yield at higher

temperatures. There was a consequent increase in gas yield. They also investigated the influence of nitrogen flow rate on product yield and found only negligible differences in yield.

Islam et al., [9] using a fixed bed reactor pyrolysed 750 gm batches of waste tire and also found a high oil yield of 55 wt.% at 475 ^{0}C pyrolysis temperature with a corresponding char and gas yield of 36 wt.% and 9 wt.%, respectively.

Banar et al. [10] reported that for pyrolysis of tire derived fuel (steel removed) the maximum oil yield was only 38.8 wt.%, with char yield at 34 wt.% and a high gas yield of 27.2 wt.% for a heating rate of 5 ^{0}C min^{-1} at a pyrolysis temperature of 400 ^{0}C

Kar [11] pyrolysed 10 gm batches of waste tires in a fixed bed, nitrogen purged reactor at 10 ^{0}C min^{-1} heating rate. The influence of pyrolysis temperature from 375 to 500 ^{0}C was investigated and it was reported that the maximum oil yield of 60 wt.% oil was obtained at 425 ^{0}C. At the higher temperature of pyrolysis, of 500 ^{0}C, the oil yield decreased to 54.12 wt.%. The gas yield increased from 2.99 to 20.22 wt.% and char yield decreased from 50.67 to 26.41 wt.% as the temperature of pyrolysis was increased from 375 to 500 ^{0}C. Product yields from the pyrolysis of tire wastes with feed stock to oil energy conversion efficiency on the basis of reator types are presented in Table 1.

Table 1. Product yield from the pyrolysis of tire wastes with feed stock to oil energy conversion efficiency

Study Nos.	Reactor type	Temp. (^{0}C)	Product yield distribution			Oil characteristics			FOECE (%)
			Oil (wt.%)	Char (wt.%)	Gas (wt.%)	GCV (MJ/kg)	Sulfur (wt.%)	Density (kg/m^3)	
Study -1 [8]	Fixed bed, batch	500	40.26	47.9	11.9	44.8	0.91	945	47.16
Study -2 [9]	Fixed bed, batch, internal fire tubes	475	55.0	36.0	9.0	39.13	-	-	64.43
Study -3 [10]	Fixed bed, batch	400	38.8	34.0	27.2	42.66	0.11	833	45.45
Study -4 [11]	Fixed bed, batch	425	60.0	30.0	10.0	42.70	1.46	992	84.03
Study -5 [12]	Fixed-bed, fire-tube heating	475	46.0	43.0	11.0	40.80	1.36	970	65.28
Study -6 [13]	Rotary kiln	500	45.1	41.3	13.6	41.70	1.54	962	56.31
Study -7 [14]	Fixed bed, batch	950	20.9	40.7	23.9	42.00	1.50	910	28.78
Study -8 [15]	Fixed bed, batch	500	42.0	47.0	11.0	39.12	-	-	49.20
Study -9 [16]	Vacuum, conical spouted bed	500	60.0	34.0	4.0	39.13	-	-	70.29
Study -10 [17]	Fluidised bed	750	31.9	38.0	28.5	40.32	-	-	37.37
Study -11 [18]	Conical spouted bed	500	62.0	35.0	3.0	40.05	-	-	72.63
Study -12 [19]	Vacuum	550	47.1	36.9	16.0	38.65	-	-	55.17

2.2. Pyrolysis of plastic waste

Several authors have studied plastics pyrolysis and have demonstrated the potentialities of this technology to process plastic wastes:

Lopez et al. [20] upgraded of chlorinated oils coming from the pyrolysis of plastic waste, in order to use them as fuel or feedstock for refineries. Two different samples of pyrolysis oils have been thermally and catalytically cracked in a 300 mL autoclave at 325 °C and the auto-generated pressure. They reported that thermal cracking converts the plastic pyrolysis heavy oils into light liquid fractions which are only composed of alkanes and aromatics. These light fractions present a very low quantity of chlorine compared to the initial oils and resemble gasoline and diesel-like products. Besides, a gaseous fraction rich in methane and with very high heating value is also produced, together with a fuel-like viscous product which remains in the autoclave. The relative proportions of each of these three fractions depend on the nature of the initial oils. Red Mud has proved to be a dehydrochlorination and cracking catalyst, since it gives rise to higher quantity of gases and light liquid fractions with a very low chlorine content (< 0.1 wt.%). Therefore, dechlorinated light oils can be obtained by Red Mud low temperature catalytic cracking of plastic derived chlorinated pyrolysis oils.

Hartulistiyoso et al. [21] investigated the temperature distribution in the reactor of a plastics pyrolysis process from waste bottles of beverage to produce fuel. The experiment was conducted using a cylindrical reactor, which has dimension of 0.31 m in diameter and 1 m high. The reactor was used to process 1500 gm plastics. They reported that to increase temperature from the ambient temperature to 450^{0}C, 72 minutes of time were needed. The lowest temperature of 310°C was measured at the top of the reactor, whereas different temperature in the middle of the reactor was found to be 46°C respectively. The pyrolysis process of 1500 gm plastics was completed in 110 minutes to produce 21 g of fuel. They concluded that the pyrolysis process of plastics can produce fuel at 450^{0}C in the reactor and 75^{0}C outside the reactor.

Muhammad et al. [22] pyrolyzed plastic waste collected from waste electrical and electronic equipment (WEEE) in the presence of zeolite catalysts to produce a gasoline range aromatic oil. They used two zeolite catalysts; Y zeolite and ZSM-5. They reported that the quantity of oil produced from uncatalysed pyrolysis of plastics was more than 80 wt%. The gases consisted of hydrogen, methane and C_2–C_4 hydrocarbons. When the zeolite catalysts were introduced there was a decrease of between 5 and 10 wt% in oil yield and a corresponding increase in gas yield. The composition of the oils derived from the uncatalysed pyrolysis of WEEE plastics were mainly aromatic with high concentrations of styrene. Addition of the zeolite ZSM-5 and Y zeolite to the pyrolysis process resulted in significant concentrations of benzene, toluene and ethylbenzene in the product oil but reduced concentrations of styrene. The oils from both thermal and catalysed pyrolysis also contained significant concentrations of polycyclic aromatic hydrocarbons for example, naphthalene, phenanthrene and pyrene.

Kumar and Singh [23] used response surface methodology (RSM) to optimize the process for catalytic pyrolysis of waste high-density polyethylene to liquid fuel over modified catalyst. The reaction temperature, acidity of the modified catalysts and mass ratio between modified catalysts to waste high-density polyethylene (HDPE) were chosen as independent variables. Face centered central composite (FCCD) design of experiment has been used. Optimum operating conditions of reaction temperature (450 °C), acidity of catalyst (0.341) and catalyst to waste HDPE ratio (1:4) were produced the maximum liquid product yield of 78.7wt%. They reported that the liquid fuel obtained by catalytic pyrolysis of waste HDPE at optimized condition consists of petroleum products range hydrocarbons (C_{10}–C_{25}) with high heating value (40.17 MJ/kg).

Syamsiro et al. [24] studied fuel oil production from municipal plastic wastes by sequential pyrolysis and catalytic reforming processes. Three kinds of municipal plastic wastes were collected from the final disposal site and the small recycling company in Yogyakarta city, Indonesia. Commercial Y-zeolite and natural zeolite catalysts were used in thir study. They reported that the feedstock types strongly affect the product yields and the quality of liquid and solid products. HDPE waste produced the highest liquid fraction. The catalyst presences reduced the liquid fraction and increased the gaseous fraction. Furthermore, municipal plastic wastes pyrolysis produced higher heating value solid products than those of biomass and low rank coal.

Pyrolysis of a mixture containing polyethylene (PE), polypropylene (PP) and polystyrene (PS) that are major plastic components of MSW in different blends, studied by Kaminsky et al. [25]. They found that total conversion in all tests was higher than 80%, the main product being liquid (at normal conditions of temperature and pressure) with yields around 75wt% and gas yields were always lower than 10%, though products yields depended on the nature of plastic input. Product yields from the pyrolysis of plastic wastes with feed stock to oil energy conversion efficiency on the basis of reator types are presented in Table 2.

Table 2. Product yield from the pyrolysis of plastic wastes with feed stock to oil energy conversion efficiency

Study Nos.	Reactor type	Feed type	Temp. (^{0}C)	Product yield distribution			Oil characteristics			FOECE (%)
				Oil (wt.%)	Char (wt.%)	Gas (wt.%)	GCV (MJ/kg)	Sulfur (wt.%)	Density (kg/m^3)	
Study -1 [22]	Catalytic	Plastic	420	61.00	-	-	43.00	-	854	136.1
Study -2[22]	Catalytic	HIPS	450	84.00	6	10	44.89	-	-	187.42
Study -3 [22]	Catalytic	RP	450	82.00	8	10	44.98	-	-	182.95
Study -4 [22]	Catalytic	ABS	450	66.50	-	-	44.50	-	-	146.79
Study -5 [23]	Catalytic	HDPE	450	78.70	-	-	40.17	-	864	100.27
Study -6 [24]	Two stage batch	HDPE	450	56.00	8	36	42.82		799	87.74
Study -7 [24]	Two stage batch	PE Bag	450	50.00	10	40	46.67	0.01	858	74.00
Study -8 [26]	Catalytic	Plastic	400	75.00	15	10	44.00			163.69
Study -9 [27]	Autoclave	Plastic	270	70.00	-	-	45.00	<0.002	793	156.25
Study -10 [28]	Hydrocracking	LDPE	450	30.64	68.27	1.10	46.00	-	-	69.91
Study -11 [29]	Semi batch fluidized	PVC	380	12.17	-	-	46.00	-	-	27.77

2.3. Pyrolysis of woody biomass waste

Lu et al. [30] investigated the catalytic performance of acidic ionic liquids (AIL) containing HSO_4^- anion and acidic-functionalized imidazolium cations for biomass liquefaction was firstly investigated in polyethylene glycol 400-glycerol mixture at atmospheric pressure in order to explore green and efficient ways to convert woody biomass into sustainable energy and chemicals. They reported that fir sawdust (10 g) was up to 99% liquefied using 60 g of solvent at a concentration of 1-(3-sulfopropyl)-3-methylimidazolium hydrogensulfate ionic liquid of 0.3 mol·L^{-1}, at a temperature of 423 K, in 60 min. The introduction of the sulfoalkyl substituent into the imidazolium cation of AILs was found to significantly improve their catalytic activity. The catalytic

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performances of 1-(3-sulfopropyl)-3-methylimidazolium hydrogensulfate and 1-(4-sulfobutyl)-3-methylmidazolium hydrogensulfate are thus similar to that of H_2SO_4 due to their double acidic sites. More than 90 wt% of the bio-oil was the heavy oil that derives from lignin.

Veses et al. [31] producced of upgraded bio-oils by catalytic pyrolysis of wood biomass in an auger reactor using low cost materials as catalysts. These materials included several clay minerals (sepiolite, bentonite and attapulgite) and an industrial waste from alumina production, known as red mud. They studied the influence of temperature (400–500 ^{0}C) and the effect of catalyst to biomass ratio (3:1–1:6, in weight) were also analysed. They reported that a temperature of 450 °C and the lowest catalyst proportion (1:6, in weight) were selected as the most appropriate to aim the pyrolysis for bio-oil production. The catalysts improved the characteristics of the obtained bio-oil as fuel (viscosity, acidity, oxygen content and calorific value). For every catalyst, the viscosity of the organic liquid fraction decreased (up to 34% in case of bentonite) while lower heating value increased (up to 20% in red mud tests). Concerning acidity, sepiolite and red mud produced a decrease in the total acid number (around 29% and 23%, respectively).

Kim et al. [32] studied fast pyrolysis of yellow poplar wood subjected to HDO (hydrodeoxygenation) for the purpose of reducing water content as well as increasing heating value. HDO was performed in an autoclave reactor at three different reaction factors: temperature (250–370 ^{0}C), reaction time (40–120 min), and Pd/C catalyst loading (0–6 wt%) under hydrogen atmosphere. After completion of HDO, gas, char, and two immiscible liquid products (light oil and heavy oil) were obtained. They reported that liquid products were less acidic and contained less water than crude bio-oil. Water content of heavy oil was ranged between 0.4 wt% and 1.9 wt%. Heating values of heavy oil were estimated between 28.7 and 37.4 MJ/kg, which was about twice higher than that of crude bio-oil. They observed that heavy oil had a lower O/C ratio (0.17–0.36) than crude bio-oil (0.71). H/C ratio of heavy oil decreased from 1.50 to 1.32 with an increase of temperature from 250 °C to 350 ^{0}C, respectively.

Zhu et al. [33] studied techno-economic analysis (TEA) to evaluate the feasibility of developing a commercial large-scale woody biomass HTL and upgrading plant. In this system, woody biomass at 2000 dry metric ton/day was assumed to be converted to bio-oil via HTL and further upgraded to produce liquid fuel. They evaluated: a state-of-technology (SOT) case with HTL experimental testing results underpinning the major design basis and a goal case considering future improvements for a commercial plant with mature technologies. They obtained the annual production rate for the final hydrocarbon product was estimated to be 42.9 and 69.9 million gallon gasoline-equivalent (GGE) for the SOT and goal cases, respectively. The minimum fuel selling price (MFSP) was estimated to be \$4.44/GGE for the SOT case and \$2.52/GGE for the goal case. Product yields from the pyrolysis of biomass wastes with feed stock to oil energy conversion efficiency on the basis of reator types are presented in Table 3.

Table 3. Product yield from the pyrolysis of biomass wastes with feed stock to oil energy conversion efficiency

Study Nos.	Reactor type	Feed type	Temp (^{0}C)	Product yield distribution			Oil characteristics			FOECE (%)
				Oil (wt.%)	Char (wt.%)	Gas (wt.%)	GCV (MJ/kg)	Sulfur (wt%)	Density (kg/m^3)	
Study -1 [31]	Auger reactor	Wood	450	48	-	-	26.80	<0.10	1195	89.76
Study -2 [32]	Autoclave	Wood	450	50	-	-	37.40	-	-	86.25
Study -3 [33]	Hydrotreating	Wood	355	40	-	-	27.00	-	-	70.00
Study -4 [34]	Fixed bed	Nut shell	500	55	35	10	19.34	0.02	900	67.32
Study -5 [34]	Fixed bed	Rice husk	450	40	46	14	20.43	-	960	49.61
Study -6 [34]	Fixed bed	Jute stick	425	50	39	11	21.09	-	1224	64.03
Study -7 [34]	Fixed bed	Sawdust	440	41	-	-	19.08	-	910	47.41
Study -8 [34]	Fixed bed	Wheat straw	500	53	-	-	17.23	-	1099	60.48
Study -9 [34]	Fixed bed	Linseed residue	400	30	-	-	33.35	-	1095	60.64
Study -10 [35]	Fluidized bed	Seed scrops	500	35	49	16	40.60	0.10	-	49.51
Study -11 [36]	Fluidized bed	Rice straw	450	40	45	15	18.34	0.30	-	49.67
Study -12 [37]	Fixed bed	Coconut shell	550	43	26	31	38.6	Nil	1090	79.49

2.4. Co-pyrolysis of organic wastes

Li et al. [38] investigated of co-pyrolysis of discarded rubber and plastics in a tube furnace. They observed that compared with the pyrolysis of rubber or plastics separately, the co-pyrolysis of rubber and plastics produced a higher oil yield with a higher oil heating value. When the mass fraction of the rubber was 60 wt%, the pyrolysis