Effect of process parameters on tire pyrolysis: a review

S Karthikeyan[1*], C Sathiskumar[2] and R Srinivasa Moorthy[3]

[1,2]Department of Chemistry, Chikkanna Government Arts College, Tirupur, 641 602, India

[3]Department of Mechanical Engineering, Eritrea Institute of Technology, Eritrea, North-east Africa

This review presents pyrolysis of scrap tires with a focus on effect of process parameters (reactor temperature, gas flow rate and catalyst-tire ratio) on yield. Three commercially important pyrolysis by-products from scrap tires are carbon residue, pyrolitic oil and pyro-gas. Pyrolysis of scrap tire starts at 250°C and gets completed at 550°C. Presence of catalysts produces lighter oil with a drastic increase in the concentration of single ring aromatics.

Introduction

Disposal of waste scrap tires is a major environmental and economical issue[1]. Out of global estimates of scrap tires (5 billion tonnes annually)[2], 40% are from China, India, South America, South-East Asia, South Africa and Eastern Europe. Recent estimates of scrap tires are: North America, 4.6; European Union[3], 3.4; Japan, 1.5; China, 1.3; and India, 0.6 million tonnes (MT). Out of total mass of waste tires, 30% can be reused / recycled as new rubber products, playgrounds, sports surfacing and rubber-modified asphalt[4]. Tires[5] have been recycled as grinding, crumbling, re-treading, reclaiming, combustion and pyrolysis. Pyrolysis offers an environmentally attractive method to decompose wide variety of wastes, including scrap tires. This review focuses on effect of process parameters (catalyst-tire ratio, operating temperature and gas flow rate) on yield of pyrolitic products.

Methods of Recycling Waste Tires: An Overview

In tire re-treading process, the remaining tread is ground away from a tire to be remolded and a new tread rubber strip is fused to the old carcass by vulcanization. Mechanical milling of tires offers production of ground rubber, which is used in asphalts, carpets, sport surfaces and children's playgrounds. Cryomechanical technology (cooling of rubber to –60° to –100°C) renders very fine powder, which can be used as reinforcements in new rubber products. However, high consumption of energy, presence of liquid nitrogen in cryomechanical process and limited market for the products are main disadvantages of the process[6]. Important methods and processes for reclaiming waste rubber are mechanical shearing process[7], thermo-mechanical reclaiming[8], reclaiming by use of various chemical agents[9], microwave reclaiming[10], ultrasonic reclaiming[11], pyrolysis of waste rubber, reclaiming by renewable resource materials and reclaiming by biotechnological processes[12]. Owing to high calorific value, scrap tires are excellent materials for energy recovery[6]. However, combustion of waste tires results in no material recovery, large capital investment, need for flue gas cleaning, CO_2 and polycyclic aromatic hydrocarbon (PAH) emissions and high operating costs. Scrap tires can also be used as fuels in cement kilns.

Tire pyrolysis (thermal decomposition in an oxygen-free environment) yield[6]: solid char, 30-40; liquid residue, 40-60; and gases, 5-20 wt%. Solid residue may be used as reinforcement in rubber industry, activated carbon or fuel. Liquid products can be used as fuel, petroleum refinery feedstock or a source of chemicals. Gaseous fraction can be used as fuel in pyrolysis process.

Pyrolysis Reactors

Vacuum Moving-Bed Process

Roy *et al*[13,14] focused on vacuum pyrolysis process; reactor development has gone through a 1 kg batch vacuum vessel, a 15 kg/h semi-continuous vacuum hearth

*Author for correspondence

E-mail: environkarthi@gmail.com

and a 200 kg/h pilot scale continuous moving bed. Advantage of vacuum process is that the evaporating volatiles can be immediately removed from reactor, which minimizes secondary reactions (thermal cracking, re-polymerization, and re-condensation). As a result, oil yield is dramatically increased at the expense of char and gas.

Hamburg Fluidized-Bed Process

In this process, an indirectly heated fluidized bed is developed with the principle objective to yield basic chemicals such as BTX and carbon black for reinforcing at 700°C[15]. Laboratory-scale plants (capacity, 0.60-3.0 kg/h) have been built followed by pilot-scale plants (capacity, 10-40 kg/h of plastic and 120 kg/h of used tires) at University of Hamburg[16,17]. Efforts have also been made at lower temperatures in order to improve oil yield and reduce energy input[5].

BBC Continuous Ablative Process

Ablative is achieved by sliding contact of rubber particles on a hot metal surface, which results in high yield of liquids. Studies[18-20] demonstrated efficient heat and mass transfer from a 50 kg/h pilot-scale reactor, operated a smaller test unit at a throughput of 10-25 kg/h, and found that liquid yields of 54 wt% can be obtained at 470-540°C with a 0.88 s residence time and a 1.3 mm feeding size. Helleur et al[21] reported that pyrolitic char with steam or carbon dioxide can be converted to activated char, which exhibited excellent product for the removal of organics and heavy metals from aqueous solutions.

Continuous Rotary Kiln Process

A rotary kiln pyrolyzer with slow rotation of inclined kiln ensures thorough mixing of waste, resulting in quality pyrolitic products. Also, residence times of solid can be easily adjusted to provide optimum conditions for pyrolysis reaction. Solid wastes of various shapes, sizes and calorific values can be fed into a rotary kiln either in batches or continuously. Typical rotary kiln plants include Kobe Steel (commercial 1 tonne/h plant), Italian ENEA Research Center Trisaia pilot-scale plant and Kassel University laboratory–scale setup[22,23]. These rotary kiln reactors widely exist in the process for pyrolysis or gasification, but technical and pilot-scale testing data availability is quite scarce.

Yield of pyrolysis oil is closely related to type of reactors used. Vacuum process[13] had a maximum oil yield (53.7 wt%) at 431°C. Hamburg fluidized – bed process[5]

produced 56.8 wt% oil at 550°C. Continuous ablative process[17,18] gave a maximum oil yield (52.9 wt%) at 450°C. Continuous rotary kiln process[22] gave oil yield (45.1 wt%) at 500°C. Different oil yields of various reactors are mainly attributed to the difference of vapor residence time in high - temperature zone in each process.

Effect of Process Parameters on Yield of Pyrolitic Products

Catalyst-Tire Ratio

Liquid products of pyrolysis[24] (mixtures of paraffins, olefins and aromatic compounds) from waste tires possess high caloric value (43 MJ/kg) and can be used directly as a fuel or added to petroleum refinery feedstock[25]. But yields of these chemicals are not adequate enough for extraction from pyrolitic oil and utilization as a chemicals feedstock[26,27]. Therefore, catalytic treatment is required to upgrade quality and quantity of liquid products obtained from pyrolysis of waste tire. Tire pyrolysis carried out in the absence of catalyst yielded oils of high boiling point[28]. Use of catalyst in pyrolysis of waste tires result in cracking down heavy hydrocarbons into lower molecular weight pyrolitic oils (Table 1). Increase in catalyst-tire ratio decreased amount of asphaltenes in pyrolitic oil[29]. Xie et al[30] found that copper nitrate as catalyst slightly increased the amount of most PAHs (phenanthrene) in pyrolytic oils, and improved specific surface area of pyrolitic char. Ates et al[31] reported that pyrolitic oil yield increased with increase of catalyst-tire ratio and reached maximum by using 10 wt% activated alumina and also its composition was richer than that of non-catalytic bio-oil. Dung et al[32] studied catalytic activity of Ru/MCM-41, and proved that high yield of light olefins for catalytic oil was four times higher than those of non-catalytic oil and that Ru/MCM-41 catalyst produced lightest oil with the highest concentration of mono-aromatics.

Using Ru/SBA-1 as a catalyst, Dung et al[33] observed that ruthenium (Ru) cluster increased twice the yield of gaseous products as compared to thermal pyrolysis. Ru clusters were active sites for polyaromatic and polar-aromatic hydrocarbon (PPAHs) reductions, leading to the production of light oils, with decreased saturates. Zhang et al[34] reported that pyrolitic oil with more dl-limonene was obtained using basic additives (NaOH, Na_2CO_3); NaOH could lower pyrolysis temperature and oil yield could be as high as 49.7 wt% at 480°C, but Na_2CO_3 did not promote pyrolysis reaction. Among basic

Table 1—Influence of some process conditions on char, liquid and gas yields under pyrolytic process

Catalyst	Catalyst ratio	Temp.	Nitrogen flow rate	Pressure	Yield, wt%		
	%	°C		Kpa	Oil	Gas	Char
Without catalyst[50]	n.d.	450-650	n.d.	n.d.	50	40	10
Without catalyst[52]	n.d.	600	n.d.	-20 to -10 pa	42.7	18	39.3
Without catalyst[48]	n.d.	390-890	Helium, 30 cm³/min	n.d.	5	73	20
Without catalyst[46]	n.d.	425-600	30 l/min	n.d.	44.5-55	1.8-6.8	33.9-35.8
Without catalyst[1]	n.d.	600	n.d.	n.d.	53.1	8.9	38
Without catalyst[13]	n.d.	480-520	n.d.	10	43-47	5-6	43-47
Without catalyst[41]	n.d.	430	n.d.	n.d.	33.3	17.7	49
Without catalyst[47]	n.d.	200-500	n.d.	10.3	61	13	26
Without catalyst[14]	n.d.	450	n.d.	2	59	5.	33.8
Y-Zeolite (CBV-780)[40]	n.d.	500	n.d.	n.d.	33.4	18.3	8
ZSM-5 (CBV-400) [40]	1.5	500	n.d.	n.d.	35.8	19.8	6.7
Zeolite USY[45]	0.25-1.0	150-500	n.d.	n.d.	31.6-12.7	30.5-49.9	n.d.
Y-type Zeolite (CBV-400)[39]	50	430-600	n.d.	n.d.	38.7-32.2	16.3-21.8	n.d.
ITQ-21, Zeolite additives[29]	HMOR+2% ITQ-21	500	30 ml/min	n.d.	41	13.8	45.2
ZSM-5[39]	50	430-600	n.d.	n.d.	34.6	15.1-20	n.d.
Y-Zeolite (CBV-400) [40]	7	500	n.d.	n.d.	32	14-20	0.2-10.1
ZSM-5[41]	n.d.	430	n.d.	n.d.	33.6	16.0	50.4
ITQ-24, Zeolite additives[29]	HMOR+2% ITQ-24	500	30 ml/min	n.d.	42.4	12	45.6
ZSM-5/LBO[41]	n.d.	430	n.d.	n.d.	48.0	9.3	42.7
LBO[41]	n.d.	430	n.d.	n.d.	33.5	14.0	52.5
$Al_2O_3+SiO_2$[28]	n.d.	400	n.d.	n.d.	14.8	5	80.13
Al_2O_3[28]	n.d.	400	n.d.	n.d.	23.2	20.93	55.67
SiO_2[28]	n.d.	400	n.d.	n.d.	22.8	15.46	56.26
CaC_2[38]	0.2	280-400	n.d.	n.d.	38.4	29.6	32
$CaCO_3$[35]	n.d.	400	n.d.	n.d.	29.2	31.9	39.06
$Ca(OH)_2$[37]	5	500	200 cm³/min	n.d.	40	12	48
Na_2CO_3[34]	n.d.	550	n.d.	3.5-10	39	20.8	40.2
NaOH[34]	n.d.	550	n.d.	3.5-10	47.8	14.6	37.6
MgO[35]	n.d.	400	n.d.	n.d.	27.0	19.33	53.5

n.d. = not determined

catalysts (MgO and $CaCO_3$)[35], MgO resulted in pyrolitic oil with 55% hydrocarbon, whereas $CaCO_3$ resulted in oil with 50% hydrocarbon. Yorgun & Simsek[36] used 60 wt% of activated alumina catalyst and found highest pyrolysis oil yield (51 wt%). Pyrolysis of waste tire in fixed batch reactor under N_2 and $Ca(OH)_2$ environment showed[37] that the highest yield of liquid product was obtained with 5% $Ca(OH)_2$ addition; $Ca(OH)_2$ acted to reduce sulfur content (34%) of liquid oil. Shah *et al*[28] observed that catalytic pyrolysis with Al_2O_3 gave higher amount of oil and less quantity of gas, mixtures of hydrocarbons were present with higher concentration of polar hydrocarbons (40%) in oil derived with Al_2O_3 and 40% aliphatic hydrocarbons in oil derived with SiO_2, and equal concentration of aliphatic (35%) and polar (35%) hydrocarbons were present in oil derived with Al_2O_3:

SiO_2 in a 1:1 ratio. Using calcium carbide as a catalyst[38] in a batch reactor under atmospheric conditions, pyrolytic liquid is obtained relatively with greater value and low boiling range in presence of catalyst as compared to pyrolysis without catalyst.

Using zeolite catalysts[39,40], Y-type zeolite catalyst of large pore size and higher surface activity was found to produce higher concentrations of aromatic compounds compared to ZSM-5 catalyst; presence of catalysts reduced oil yield with a consequent increase in gas yield and formation of coke on the catalyst. Wei Qu *et al*[41] observed that a kind of lubricant base oil (LBO) can enhance catalytic effects of pyrolysis of waste tires over ZSM-5 zeolite; compared to pyrolysis without LBO, catalytic co-pyrolysis with LBO shows a sharply increased catalytic degradation rate and the liquid yield

increase, whilst gas yield and residue yield decrease. Dung et al[29] observed that ITQ-21 and ITQ-24 as zeolite additives have strong effect on catalytic pyrolytic oil using HMOR. As compared with the case of pure HMOR, adding ITQ-21 enhanced production of kerosene, whereas introduction of ITQ-24 result in higher concentration of aromatic compounds in derived oil. With respect to HMOR, ITQ-24 as an additive resulted in higher concentration of aromatics whereas adding ITQ-21 decreased concentration. Boxiong et al[26] showed that the presence of zeolite USY catalyst reduce oil yield with consequent increase in gas yield. Olazer et al[42] studied effect of acid catalysts based on HZSM -5, HY and H Beta zeolites on the distribution of volatile products in pyrolysis of tire material carried out in a fast heating micro-reactor, and observed that acid catalyst allows carrying out tire pyrolysis at 723 K with complete conversion in 60 s.

Abdul Raouf et al[43] used $AlCl_3$, Al_3O_2 and $CaCl_2$ as a catalyst, and observed that Al_3O_2 gave highest paraffin at any ratio and at any temperature in the order $Al_3O2 > AlCl_3 > CaCl_2$. San Miguel et al[44] investigated catalytic activity of five different acid catalyst [three acid zeolites (ZSM-5, nanocrystaline ZSM-5 and bete) and two meso-structured materials (Al-MCM-41 and Al-SBA-15)] on thermal conversion of used tire, and found that all zeolite materials showed a marked selectivity towards the formation of aromatic species, particularly toluene (up to 19.82%), m/p-xylene (up to 16.91%) and benzene (up to 10.28%); meso-structured catalysts not only exhibited strong aromatization properties, but also a marked alkylation capacity, resulting in the formation of a wider range of alkyl-aromatic products.

Operating Temperature and Gas Flow Rate

Temperature and gas flow rate have a major influence on the yield of tire pyrolysis (Table 1). Boxiong et al[45], using USY zeolite catalyst, observed that heating rate for pyrolysis reactor was 5-40°C/ min, preheated temperature for pyrolysis reactor was 150°C, and final temperatures was 550°C; optimum yield of oil was 32.7 wt% at 500°C. Cunliffe & Williams[1] showed that oil yield reached a maximum of 58.2 wt% at 475°C and decreased gradually to 53.1 wt% at 600°C. Lopez et al[46] studied continuous pyrolysis (feed rate, 30 l min⁻¹; temp., 425-600°C) of scrap tire in a conical spouted bed controlled, and found following yields: gases, 1.8-6.8; liquid fraction, 44-55; and char, 33.9-35.8 wt%. However, Qu et al[41] studied catalytic co-pyrolysis of waste tires

over ZSM- 5 zeolite with LBO at 430°C under nitrogen atmosphere, and found following yields: gases, 17.7; liquid fraction, 33.3; and char, 49.0 wt%. Mirmiran et al[47] attempted vacuum pyrolysis of waste tire at 200-500°C and below 10.3 kPa absolute pressure, and found following yields: gases, 13; oils, 61; and char, 26%. Zabaniotou et al[48] studied tire pyrolysis at 390-890°C, with heating rates of 70-90°C s⁻¹ at atmospheric pressure, under helium (He), and observed that char yield decreased to 20wt% of raw material with temperature reaching an asymptotic value of 830°C. Murillo et al[49] conducted pyrolysis experiment (heating rate, 10°C/min; N flow rate, 100 ml/min; temp., 375-500°C) to check influence of temperature on yield of products at every 35°C, and observed that with increase in temperature (375-500°C), gas yield continuously increased (2.99-20.22 wt%), char yield decreased from 50.67 to 26.41 wt% at 450°C and then remained almost constant, and oil yield increased from 42.24 wt% to a maximum of 60.02 wt% at 425°C and then decreased to 54.1 wt% at 500°C.

In an experimental work[50] (temp., 450-650°C; heating rate, 5°C/min; residence time of feedstock in reactor, 120 min), tire pyrolysis products as vapor were water cooled to yield following products: pyrolysis oil, 55; pyro-gas, 10; and moisture, 1%. Crude tire pyrolysis oil (TPO) thus obtained had a higher viscosity and sulphur content compared to diesel fuel, but TPO blended with diesel could be used as an alternate fuel for diesel engines.

Shah et al[35,38] observed that catalytic pyrolysis using $CaCO_3$ and MgO as catalyst gave maximum oil (39 wt%) at 350°C. Dung et al[32] in tire pyrolysis (temp., 350°C) using catalysts (MCM-41 and Ru/MCM-41, respectively) showed: solid, 45, 45; liquid, 38, 25; and gas, 15%, 30%. Keeping pyrolysis conditions constant, tire was completely decomposed at 500°C[51]. Zhang et al[34] observed that catalytic pyrolysis of granules of waste tires using NaOH under vacuum (3.5-10 kPa) conditions at 480°C gave highest oil yield (49.7 wt%). Roy et al[14] found that thermal decomposition of rubber gave maximum yield of oil (55%; specific gravity, 0.95; gross heating value, 43 MJ/kg) at 415°C below 2 kPa. In another pyrolysis process[13] (temp., 480-520°C; total pressure, < 10 kPa), typical yield of vacuum pyrolysis process were: carbon black, 36-39; oil, 43-47; and gas, 5-6 wt%. Oil yield with vacuum process is higher than the oil yield from an atmospheric pyrolysis process, whereas yields of carbon black and gas, respectively, are lower. Pilot scale pyrolysis in a continuous rotary kiln reactor[52] (pressure, -20 to -10

Pa) gave maximum oil yield (45 wt%) at 500°C. Pyrolysis (N flow rate, 0.47 l/min) of tire-derived fuels[53] (TDFs) yielded a complex mixture of hydrocarbons in pyrolysis oil along with gaseous and char products. Maximum oil yield was found at heating rate of 5°C/min; quantities of by products reached maximum concentration at 500°C. Islam *et al*[54] observed that tire pyrolysis (feedstock size, 5-7 cm; running time, 75 min) in fixed reactor bed, under N_2 atmosphere, gave maximum yields at 450°C as follows: char, 30; liquid, 61; and gas, 9%. Heating value of oil was quite high, almost similar to diesel fuel.

Pyrolysis oil derived from waste tires is not appropriate for direct use in combustion process due to its high sulphur content[55]. During combustion, sulphur in the fuel form sulphur oxides. Since SO_2 is very corrosive, sulphur content of fuel is limited[13]. Bunthid *et al*[55] observed that addition of formic acid (pH 4.0) in presence of 25 vol% of hydrogen peroxide (H_2O_2) and tire pyrolysis char enhanced the level of sulphur removal to 70% due to simultaneous adsorption and oxidation of sulfurous compounds on the surface of pyrolysis char. Trongkaew *et al*[56] achieved a maximum sulphur removal of 43.6% by applying photo assisted oxidation catalyzed by titanium dioxide (TiO_2, Degussap - 25) to partially remove sulphurous compounds in waste tires pyrolysis oil under milder reaction condition without hydrogen consumption. Witpathomwong *et al*[57] investigated waste tire pyrolysis using MCM-48 and Ru/MCM - 48 as catalysts, and showed that Ru/MCM-48 insignificantly reduced the amount of sulphur in oil. This indicates mild cracking activity of MCM-48 and low activity of Ru on breaking C-S bonds in pyrolitic oil. However, when crude tyre pyrolysis oil was treated with known volume of concentric hydrosulphuric acid (8%), maximum removal of sulphur was achieved[58].

Conclusions

Pyrolitic oil is mainly used directly as a fuel or added petroleum refinery feedstock. Catalysis leads to substantial increase in amount of gases and a consequent decrease in the amount of liquids, due to stronger thermal cracking produced at higher temperatures. Increasing catalyst to tire ratio decreased the amount of asphaltenes in pyrolitic oil. However, there is not much difference in the amount of asphaltenes obtained from the case of catalyst-to-tire ratio of 0.25-0.33. Increasing catalyst feed ratio results in increase of alkaline gases (methane and ethane). Gas yield remains almost constant in

catalyst-tire ratio range of 0.00-0.10 and then markedly increases, due to more materials get cracked into uncondensed gaseous products and cracking activity is enhanced with increase of catalyst-to-tire ratio. Larger catalyst pore size results in higher concentration of aromatics. Aromatic species had a greater pre-disposition to being involved in hydrogen transfer and cyclization reactions. Catalytic pyrolysis contains lower amount of olefins and slightly higher amount of aromatics and paraffin's than non-catalytic pyrolysis oils. Also, liquid obtained is relatively in greater volume and low boiling range in presence of catalyst as compared to pyrolysis in the absence of catalyst. Sequence of type of catalyst that shifts reaction towards the yield of pyrolitic oil is: without catalyst > basic catalyst > acid catalyst. Increasing pyrolysis temperature results in an increase in aromatic content of oils with consequent decrease in aliphatic content. Pyrolysis temperature beyond 375°C lead to decrease of liquid content in most of the pyrolysis processes.

References

1   Cunliffe A M & Williams P T, Composition of oils derived from the batch pyrolysis of tires, *J Anal Appl Pyrolysis,* **44** (1998) 131-152.

2   Kar Y, Catalytic pyrolysis of car tire waste using expanded perlite, *Waste Manage*, **31** (2011) 1772-1782.

3   Elbaba I, Wu C & Williams P T, Catalytic pyrolysis gasification of waste tyre and tyre elastomers for hydrogen production, *Energy Fuels*, **24** (2010) 3928-3935.

4   Elbaba I, Wu C & Williams P T, Hydrogen production from the pyrolysis gasification of waste tires with a nickel/cerium catalyst, *Int J Hydrogen Energy,* **36** (2011) 6628-6637.

5   Kaminsky W & Mennerich D, Prolysis of synthetic tire rubber in a fluidized-bed reactor to yield 1,3-butadiene, styrene and carbon black, *J Anal Appl Pyrolysis*, **803** (2001) 58-59.

6   Juma M, Korenova Z, Markos J, Annus J & Jelemensky L, Pyrolysis and combustion of scrap tire, *Pet Coal,* **48** (2006) 15-26.

7   Phadke A A, Bhattachary A K, Chakraborty S K & De S K, Studies of vulcanization of reclaimed *rubber*, *Rubber Chem Technol,* **56** (1983) 726-735.

8   Harshaft A A, Solid waste treatment technology, environment science technology *Environ Sci Technol*, **6** (1972) 412-421.

9   Saville B & Watson A A, Structural Characterization of Sulfur-Vulcanized Rubber Networks, *Rubber Chem Technol,* **40** (1967) 100-148.

10   Fix S R, Microwave devulcanization of rubber, *Elastomerics,* **112** (1980) 38-40.

11   Isayev A I, Yushanov S P & Chen J, Ultrasonic Devulcanization of Rubber Vulcanizates Part 1: Process Model, *J Appl Polym Sci*, **59** (1996) 803-813.

12 Adhikari B, De D & Maiti S, Reclamation and recycling of waste rubber, *Prog Polym Sci,* **25** (2000) 909-948

13 Roy C, Chaala A & Darmstadt H, The vacuum pyrolysis of used tires: End-uses for oil and carbon black products, *J Anal Appl Pyrolysis*, **51** (1999) 201-221.

14 Roy C, Labrecque B & De Caumia B, Recycling of scrap tyres to oil and carbon black by vacuum pyrolysis, *Resour Conserv Recycl,* **4** (1990) 203-213.

15 Kaminsky W & Shin H, Pyrolysis of plastic waste and scrap tyres using a fluidised bed process, in *Thermal Conversion of Solid Waste and Biomass*, *ACS Symp Ser 130*, edited by J L Jones & S B Radding (American Chemical Society, Washington D C) 1980, 423-433.

16 Kaminsky W, Chemical recycling of mixed plastics by pyrolysis, *Adv Polym Tech,* **14** (1995) 337-344.

17 Grittner N, Kaminsky W & Obst G, Fluid bed pyrolysis of anhydride hardened epoxy resins and polyester-polyurethane by the hamburg process, *J Anal Appl Pyrolysis,* **25** (1993) 293-299.

18 Black J W, Brown D B, G & Bridgwater A V, Preliminary mass balance testing of the continuous ablation reactor, in *Biomass Thermal Processing, Proc of First Canada/European Community R&D Contractors' Meeting*, edited by E Hogan & J G Robert (CPL Press, Ottawa, Canada) 1990, 123-125.

19 Brown D B, Continuous ablative regenerator systems, Bio-oil production and utilisation, in *Proc 2nd EU-Canada Workshop of Thermal Biomass processing,* edited by A V Bridgwater & E N Hogan (CPL Press, Berkshire, UK) 1996, 96-101.

20 Bridgwater A V & Peacocke G V C, Fast pyrolysis processes for biomass, *Renewab Sustain Energy Rev*, **4** (2000) 1-73.

21 Helleur R, Popovic N, Ikura M, Stanciulescu M & Liu D, Characterization and potential applications of pyrolitic char from ablative pyrolysis of used tires, *J Anal Appl Pyrolysis*, **813** (2001) 58-59.

22 Fortuna F, Cornacchia G, Mincarini M & Sharma V K, Pilot-scale experimental pyrolysis plant: mechanical and operational aspects, *J Anal Appl Pyrolysis,* **403** (1997) 40-41.

23 Klose W & Wiest W, Experiments and mathematical modeling of maize pyrolysis in a roatry kiln, *Fuel*, **78** (1999) 65-72.

24 Islam M R, Haniu H & Fardoushi J, Pyrolysis kinetics behavior of solid tire wastes available in Bangladesh, *Waste Manage*, **29** (2009) 668-677.

25 Dai X, Yin X, Wu C, Zhang W & Chen Y, Pyrolysis of waste tires in a circulating fluidized-bed reactor, *Energy,* **26** (2001) 385-399.

26 Boxiong S, Chunfei W, Cai L, Binbin G & Rui W, Pyrolysis of waste tyres: the influence of USY catalyst/tyre ratio on products, *J Anal Appl Pyrolysis,* **78** (2007a) 243-249.

27 Boxiong S, Chunfei W, Binbin G, Rui W & Cai L, Pyrolysis of waste tyres with zeolite USY and ZSM-5 catalysts, *Appl Catal B,* **73** (2007) 150-157.

28 Shah J, Jan M R & Mabood F, Recovery of value-added products from the catalytic pyrolysis of waste tyre, *Energy Convers Manage*, **50** (2009) 991-994.

29 Dung N A, Mhodmonthin A, Wongkasemjit S & Jitkarnka S, Effects of ITQ- 21 and ITQ- 24 as zeolite additives on the oil products obtained from the catalytic pyrolysis of waste tire, *J Anal Appl Pyrolysis*, **85** (2009) 338-344.

30 Xie Q C, Bao W R, Huang W & Zhao J B, Pyrolysis of waste tires with copper nitrate, *Energy Sources,* **26** (2004) 397-407.

31 Ates F, Putun A E & Putun E, Fixed bed pyrolysis of Euphorbia rigida with different Catalysts, *Energy Convers Manage,* **46** (2005) 421-432.

32 Dung N A, Klaewkla R, Wongkasemjit S & Jitkarnka S, Light olefins and light oil production from catalytic pyrolysis of waste tire, *J Anal Appl Pyrolysis,* **86** (2009) 281-286.

33 Dung N A, Walairat T, Wongkasemjit S & Jitkarnka S, Roles of ruthenium on catalytic pyrolysis of waste tire and the changes of its activity upon the rate of calcinations, *J Anal Appl Pyrolysis,* **87** (2010) 256-262.

34 Zhang X, Wang T, Ma L & Chang J, Vacuum pyrolysis of waste tires with basic additives, *Waste Manage*, **28** (2008) 2301-2310.

35 Shah J, Jan M R & Mabood F, Catalytic pyrolysis of waste tyre rubber into hydrocarbons via base catalysts, *Iran J Chem Chem Eng*, **27** (2008) 103-109.

36 Yorgun S & Simsek Y E, Catalytic pyrolysis of Miscanthus giganteus over activated alumina, *Biores Technol,* **99** (2008) 8095-8100.

37 Cumali Ýlkýlýç & Hüseyin Aydýn, Fuel production from waste vehicle tires by catalytic pyrolysis and its application in a diesel engine, *Fuel Process Technol,* **92** (2011) 1129 -1135.

38 Shah J, Jan M R & Mabood F, Catalytic conversion of waste tires into valuable hydrocarbons, *J Polym Environ,* **15** (2007) 207-211.

39 Williams P T & Brindle A J, Catalytic pyrolysis of tyres: influence of catalyst temperature, *Fuel*, **81** (2002) 2425-2434.

40 Williams P T & Brindle A J, Aromatic chemicals from the catalytic pyrolysis of scrap tyres, *J Anal Appl Pyrolysis,* **67** (2003) 143-164.

41 Qu W, Zhou Q, Wang W Z, Zhang J, Lan W, *et al*, Pyrolysis of waste tire on ZSM-5 zeolite with enhanced catalytic activities, *Polym Degrad Stab,* **91** (2006) 2389-2395.

42 Olazar M, Arabiourrutia M, López G, Aguado R & Bilbao J, Effect of acid catalysts on scrap tyre pyrolysis under fast heating conditions, *J Anal Appl Pyrolysis,* **82** (2008) 199-204.

43 Abdul-Raouf M E, Maysour N E, Abdul-Azim A A & Amin M S, Thermochemical recycling of mixture of scrap tyres and waste lubricating oil into high caloric value products, *Energy Convers Manage*, **51** (2010) 1304-1310.

44 Sanmiguel G, Aguado J, Serrano D P & Escola J M, Thermal and catalytic converson of used tyre rubber and its polymeric constituents using by –GC/MS, *Appl Catal B,* **64** (2006) 209-219.

45 Boxiong S, Chunfei W, Rui W, Binbin G & Cai L, Pyrolysis of scrap tyres with zeolite USY, *J Hazard Mater,* **B137** (2006) 1065-1073.

46 Lopez G, Olazar M, Aguado R & Bilbao J, Continuous pyrolysis of waste tyres in a conical spouted bed reactor, *Fuel,* **89** (2010) 1946-1952.

47 Mirmiran S, Pakdel H & Roy C, Characterization of used tire vacuum pyrolysis oil: nitrogenous compounds from the naphtha fraction, *J Anal Appl Pyrolysis,* **22** (1992) 205-215.

48 Zabaniotou A A & Stavropoulos G, Pyrolysis of used automobile tires and residual char utilization, *J Anal Appl Pyrolysis,* **70** (2003) 711-722.

49 Murillo R, Aylon E, Navarro M V, Callen M S, Aranda A & Mastral A M, The application of thermal processes to volarise waste tyre, *Fuel Process Technol,* **87** (2006)143-147.

50 Murugan S, Ramaswamy M C & Nagarajan G, The use of tyre pyrolysis oil in diesel engines, *Fuel Process Technol,* **90** (2008) 67-74.

51 Berrueco G C, Esperanza E, Mastral F J, Ceamanos J & Garcýa-Bacaicoa P, Pyrolysis of waste tyres in an atmospheric static-bed batch reactor: Analysis of the gases obtained, *J Anal Appl Pyrolysis*, **74** (2005) 245-253.

52 Li S Q, Yao Q, Chi Y, Yan J H & Cen K F, Pilot-scale pyrolysis of scrap tires in a continuous rotary kiln reactor, *Ind Eng Chem Res,* **43** (2004) 5133-5145.

53 Unapumnuk K, Lu M & Keener T C, Carbon distribution from the pyrolysis of tire- derived fuels, *Ind Eng Chem Res*, **45** (2006) 8757-8764.

54 Islam M N, Khan M F R & Alam M Z, Production and characterization of scrap tyre pyrolysis oil and its blend, in *Proc of Int Conf on Mech Engg* (Bangladesh univ of Engg & Technol, Dhaka, Bangladesh) 26-28 December 2003.

55 Bunthid D, Prasassarakich P & Hinchiranan N, Oxidative desulfurization of tire pyrolysis naphtha in formic acid/ H_2O_2/ pyrolysis char system, *Fuel,* **89** (2010) 2617-2622.

56 Trongkaew P, Utistham T, Reubroycharoen P & Hinchiranan N, Photocatalytic desulfurization of waste tire pyrolysis oil, *Energies,* **4** (2011) 1880-1896.

57 Witpathomwong C, Longloilert R, Wongkasemjit S & Jitkarnka S, Improving light olefins and light oil production using Ru/MCM-48 in catalytic pyrolysis of waste tire, *Energy Procedia*, **9** (2011) 245-251.

58 Murugan S, Ramaswamy M C & Nagarajan G, Performance, emission and combustion studies of a DI diesel engine using distilled tyre pyrolysis oil – diesel blends, *Fuel Proess Technol,* **89** (2008) 152-159.