

Catalytic Pyrolysis of Waste Tyre Rubber into Hydrocarbons Via Base Catalysts

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ABSTRACT: *The waste tyres represent a source of energy and valuable hydrocarbon products. Waste tyres were pyrolysed catalytically in a batch reactor under atmospheric pressure. The effects of basic catalysts (MgO and CaCO₃) were studied on the pyrolysis products. The distribution ratio of gas, liquid and char with MgO and CaCO₃ were 24.4:39.8:35.8 wt % and 32.5:32.2:35.2 wt % respectively at 350 °C for 2hr catalytic pyrolysis. The physical and chemical properties of the pyrolyzed products obtained were characterized. Both catalysts produced 25 % wt of aliphatic hydrocarbons but with the use of magnesium oxide the aromatic hydrocarbons increased (55 %) and polar hydrocarbons decreased (20 %) as compared to calcium carbonate catalyst (50 % aromatic and 25 % polar hydrocarbons). As far as the distillation data and fuel tests are concerned, the oil fractions with both catalysts fulfill the present specifications of diesel fuel commercial products.*

KEY WORDS: *Tyre, Catalytic pyrolysis, Magnesium oxide, Calcium carbonate.*

INTRODUCTION

The negative environmental impacts caused by disposal of waste automotive tyres in landfills or by incineration can be reduced by recovery of constituent chemicals and energy content by a number of available technologies. The conventional methods for energy recovery are based on simple combustion in cement kilns. Also, tyre powder is often used as compounding for low-value rubber goods. However, all these combined applications do not solve the waste tyre-stockpiling problem and does not result in adequate profitability. Tyre pyrolysis at present is an interesting and challenging area of research.

A number of studies have been reported in literature related to tyre pyrolysis for its conversion into valuable

compounds. *William and Brindle* used fixed bed [1-3] and fluidized bed [4,5] reactors to maximize the selective determination of single ring aromatic hydrocarbons. *Ucar et al.* [6] pyrolyzed car tyre and truck tyre in a fixed bed reactor and reported that tyre pyrolysis liquids were lighter than diesel but heavier than naphtha. *Laresgoiti et al.* [7], *Rodrigues et al.* [8], *Mastral et al.* [9] and *Diez et al.* [10] pyrolyzed waste tyres into valuable liquid fuels and compared the results of tyre oil with commercial petroleum hydrocarbons. Vacuum pyrolysis experiments were carried out by *Roy et al.* [11] and the data obtained indicated that the light fraction of pyrolytic oil may be used as gasoline additives, the middle fraction as a plasticizer in rubbers and heavy fraction for the

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production of good quality feed stock. Roy and Chaala [12] applied the same process using high temperature and reported high heating values of the pyrolysis gases. Similarly Zolezzi *et al.* [13] used fast pyrolysis method and obtained high yield of oil with high heating values.

The objective of the present study was to convert waste tyres catalytically using solid base catalysts at relatively low temperature into liquid hydrocarbons as well as to derive liquid in the boiling range of commercial fuel oil. In the literature solid acid catalysts (zeolites) are reported for catalytic pyrolysis of tyre [1, 3-5]. In the present study two basic catalysts, MgO and CaCO₃ were investigated to determine their influence on the yield and composition of the derived liquids.

EXPERIMENTAL

Material and Methods

The sample was produced from a waste tyre by extraction of the fiber and steel. For catalytic pyrolysis, representative samples of the whole tyre in 5-10 mm wide pieces were used. The pyrolysis experiments were carried out in a pyrex glass batch reactor under atmospheric pressure. A fixed amount of waste tyre rubber and catalyst (MgO/CaCO₃) was loaded in a reactor and heated at 350 °C for 2 hrs. Heating was via an external electrical heater and temperature was monitored using thermo-couple. The gaseous products passed through a trap, where the liquid hydrocarbons were collected. Liquid and solid (carbon black) pyrolysis yield were determined for each experiment by weighing the amount of each obtained and calculating the corresponding percentage. The gas yield was determined by difference.

Determination of physicochemical properties of the liquid product

The chromatographic analysis of liquid product was carried out on a Shimadzu GC-14A equipped with a flame ionization detector. Separations were carried out on a fused-silica capillary column of 25 m × 0.53 mm i.d with film thickness of 0.15 μm. The temperature was programmed from 40 to 300 °C at a rate of 5 °C/min. The detector and injector temperature was 350 and 300 °C, respectively.

Infrared spectroscopy was used for identification of liquid product measuring absorption from 400 to 4400 cm⁻¹. Phenols and carbonyls were quantitatively

determined by spectrophotometric methods using folin-denis and phenyl hydrazine reagents, respectively.

The liquid column chromatography was used to separate the different groups of hydrocarbons present in the derived liquid. Silica gel 60 (63-200 μm grain size, supplied by Merck) was packed into borosilicate glass column and the pyrolysis liquid applied to the top of the column. The column was then eluted with n-hexane, benzene and methanol to produce aliphatic, aromatic and polar fractions of the pyrolysis liquid, respectively.

Fractional distillation was carried out to separate different boiling point hydrocarbon fractions from the liquid derived from catalytic pyrolysis of waste tyre rubber. The liquid was distilled at a specific temperature until no more distilled products were collected. The fractions obtained by this method were characterized using density, refractive index, refractive index parameter (I) and refractivity intercepts (RI). The refractive indices were calculated with Abbe's refractometer (P20-Warsaw, Poland) at 20 °C. Refractive index parameter (I) and refractivity intercepts (RI) were calculated for all the fractions by using the formulas:

$$\text{Refractive index parameter (I)} = \eta^2 - 1 / \eta^2 + 2$$

$$\text{Refractivity Intercept (RI)} = \eta - d/2$$

$$\eta = \text{Refractive index, } d = \text{density.}$$

Some physical properties of pyrolytic liquids were determined by using the following standard methods: Flash point was determined by Cleveland open cup method IP-36/84 and ASTM-D92-78. Density IP-59/82, API gravity IP-160/87 and ASTM-D1298-85, Kinematic viscosity IP-711/87 and ASTM-D445-87 and Distillation IP-191/83 and ASTM-D216-77 were determined according to IP and ASTM standard methods for fuel. Gross calorific value was determined using Gallenkamp Auto Bomb Calorimeter (England).

RESULTS AND DISCUSSION

Reaction mechanism

Thermal pyrolysis of tyre rubber starts with a random initiation to form polymer radicals, but the catalytic pyrolysis on solid basis is initiated by abstraction of H⁺ from the reactants to form anionic intermediates called carboanions. The surface O²⁻ ions of metal oxides abstract H⁺ and the metal cations stabilize the carboanions [14]. The formations of anionic species indicate the existence of an electron or electron pair donating sites on the surface.

Table 1: Effect of temperature on product distribution from catalytic pyrolysis of used tyres.

Temp. (°C) Reaction product, (wt%)	MgO catalyst			CaCO ₃ catalyst		
	300	350	400	300	350	400
Gas	6.4± 0.2	13.7± 0.15	19.33± 0.31	19.3± 0.3	27.46± 0.15	31.9± 0.159
Oil	4.83± 0.06	34.06± 0.12	27.0± 0.2	1.76± 0.012	30.2± 0.036	29.2± 0.013
Solid	88.7± 0.31	52.2± 0.23	53.5± 0.23	65.93± 0.057	42.33± 0.251	39.06± 0.901

Table 2: Effect of time on product distribution from catalytic pyrolysis of used tyres at 350 °C.

Reaction product, (wt%) Time (hrs)	MgO catalyst			CaCO ₃ catalyst		
	Gas	Liquid	solid	Gas	liquid	solid
0.5	7.2± 0.2	17.13± 0.42	75.13± 0.70	13.23± 0.64	10.5± 0.50	76.26± 0.25
1.0	13.7± 0.15	34.06± 0.12	52.2± 0.23	27.46± 0.25	30.2± 0.11	42.33± 0.15
1.5	18.3± 0.3	34.53± 0.5	43.13± 0.76	30.1± 0.25	31.6± 0.12	38.26± 0.28
2.0	24.4± 0.2	39.8± 0.2	35.8± 0.2	32.53± 0.25	32.23± 0.25	35.23± 0.50

Further reaction of base catalyzed pyrolysis is similar to thermal pyrolysis. The empirical β rule states that C-C bond scission occurs at the C-C bond located β to the carbon atom having the unpaired electron. Base catalyzed reactions occurring over metal oxides are generally isomerization, addition, decomposition, alkylation and esterification etc. [15].

Yield of the pyrolysis products

The effect of temperature on product distribution from pyrolysis of used tyres using magnesium oxide (MgO) and calcium carbonate (CaCO₃) catalysts are presented in table 1. It can be seen that product distributions of both catalysts changed significantly with increasing the temperature from 300 to 400 °C. The gas yield increased with increase in temperature but the increase is greater with CaCO₃ catalyst as compared to MgO. The maximum yield of liquid obtained at 350 °C with both catalysts and further increase in temperature led to decrease in the yield of liquid. For example, with MgO as the catalyst the total gas yield increased from 13.7 to 19.3 wt % and liquid yield decreased from 34.0 to 27.0 wt % as the temperature of the catalytic pyrolysis increased from 350 to 400 °C. With CaCO₃, lower yield of liquid and higher yield of gas was obtained as compared to the MgO catalyst.

Mastral et al. [9] reported 375 °C as an optimum temperature for tyre recycling using hydro conversion

technique into maximum liquid yields. On the other hand, some authors [1,4,7,8] reported 500 °C as an optimum temperature for tyre pyrolysis. Therefore concerning catalytic pyrolysis yields, it can be concluded that 350 °C is the optimum temperature for recycling tyres. A temperature higher than 350 °C does not imply a conversion because the maximum possible conversion has already been achieved at this temperature.

The two catalysts could be easily compared at 350 °C for equivalent amount of catalyst for a 2hr catalytic pyrolysis time (table 2). The results show an increase in liquid yield that is 39.8 wt %, gas yield increases up to 24.4 wt % and coke about 9 wt % with MgO catalyst. Liquid yield with the CaCO₃ catalyst was 32.23 wt %, gas yield 32.53 wt % and coke found on the catalyst was nearly 4 wt %. The formation of the coke on the two catalysts was significant. All of the classes of compounds are involved to a greater or lesser extent in the formation of coke, for example, aromatic hydrocarbons, naphthenes, alkenes and alkanes.

Fuel characteristics of pyrolytic oils

The pyrolytic oils obtained from the catalytic pyrolysis of used tyre were characterized in terms of fuel characteristics. Some properties of pyrolytic oils are shown in table 3. For comparison purpose, the fuel properties of commercial diesel are also presented in

table 3. Specific gravity, viscosity and Kinematic viscosity of oils from both catalytic pyrolysis lie in the range of diesel fuel. The flash point of oil using CaCO_3 catalyst was close to the flash point of diesel fuel but the flash point of oil using MgO as a catalyst is lower than that of diesel fuels. The sulphur content in both oils is close to the sulphur content of diesel fuel.

The gross calorific value (GCV) and net calorific value (NCV) of pyrolytic oils are almost the same as the value for commercial diesel. The same results for GCV (42 MJ/KG) have been reported by other authors with thermal pyrolysis [6-8, 12]. The results shows that the oil derived from catalytic pyrolysis of waste tyre rubber have higher calorific values than the used tyres from which it is recovered (33 MJ/KG) [16]. These liquids have a higher calorific value than that of bituminous coal (28 MJ/KG) [17] and wood charcoal (30 MJ/KG) [18]. Therefore, both types of oils derived from catalytic pyrolysis of waste tyre, as a whole, can be used as fuel for combustion systems in industry.

Distillation test carried out at atmospheric pressure for the oils obtained from catalytic pyrolysis of waste tyre with MgO and CaCO_3 catalysts at 350 °C is shown in Fig 1. It can be seen from figure that the oil derived from catalytic pyrolysis with both catalysts has a wide boiling point range. With MgO catalyst, oil contained about 40 % gasoline fraction (boiling point range <170 °C) and 60 % diesel fraction (boiling point range 180-340 °C), same results have been reported by Ucar et al. [6] at 550 °C. Whereas gasoline fraction in oil derived with CaCO_3 catalyst is only 10 % and 90 % diesel fraction. Laresgoiti et al. [7] and Rodriguez et al. [8] obtained 13 % of such oil (b.p. <170 °C) from tyre pyrolysis at 500 °C. It should also be noted that the initial boiling point of oil derived with MgO (80 °C) was lower than that of diesel fuel but higher in the case of oil derived with CaCO_3 catalyst (128 °C). It can be concluded that the oil derived from catalytic pyrolysis can be blended with the diesel fuels.

Fractional Distillation

Hydrocarbon groups generally found in tyre derived pyrolytic oil fractions are paraffinic, naphthenic, aromatic and olefinic. The quality and characteristics of tyre derived pyrolytic oil mainly depend on the types of compounds in the mixture. Knowledge of the composition of these mixtures is important in the evaluation of the

Table 3: Some properties of pyrolytic oil from catalytic pyrolysis of used tyre at 350 °C.

Parameter	Oil derived with MgO	Oil derived with CaCO_3	Commercial Diesel
Specific gravity, (gcm^{-3})	0.840	0.864	0.82-0.86
Viscosity, (centipoises)	1.96	3.85	2.0-4.5
Kinematic viscosity, (mm^2S^{-1})	2.35	4.46	5.0
Flash point, (°C)	38	60	>55
Sulphur, (%)	0.6	0.55	< 0.70
Gross calorific value (GCV) (MgKg^{-1})	45.9	45.9	45.7
Net calorific value (NCV) (MgKg^{-1})	43.1	43.1	42.9
Boiling range (°C)	110-300	160-345	180-370

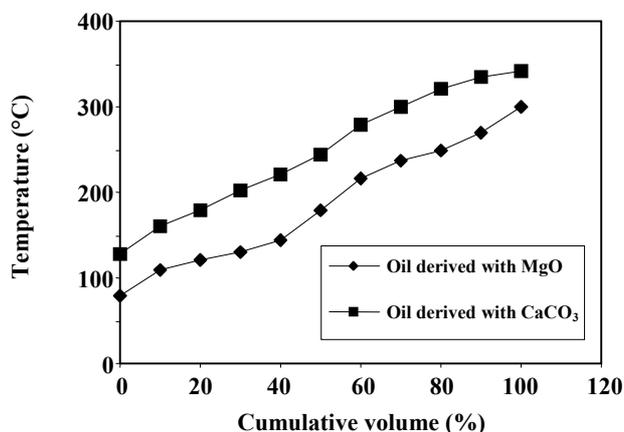


Fig. 1: Simulated distillation curves of oils derived from catalytic pyrolysis of waste tyre at 350 °C.

quality of pyrolytic oil. The hydrocarbon groups of the tyre derived oil having a boiling range of 80-300 °C were separated into different boiling point range by fractional distillation of the tyre derived oil. Refractive index (η_{20}^D) and density (d_{20}) measurements were used for the identification of hydrocarbon group types. The results are given in tables 4 and 5 for MgO and CaCO_3 catalysts, respectively. The densities and refractive indices of oil increased from 0.6588-0.929 g/cm^3 and 1.414-1.545 using MgO catalyst and from 0.6864-0.8438 g/cm^3 and 1.4350-1.5010 with CaCO_3 catalyst. There is pronounced

Table 4: Physical properties of different fractions of oil derived from the catalytic pyrolysis of used tyre (MgO).

Temp. (°C)	η_{20}^D	D_{20} , gcm ⁻³	Refractivity intercept (RI)	Refractive index parameter (I)
i.b.-100	1.414	0.6588	1.084	0.250
100-150	1.4530	0.7288	1.0886	0.270
150-180	1.4615	0.7860	1.0685	0.275
180-200	1.4800	0.8848	1.0376	0.284
200-250	1.4934	0.9130	1.0369	0.291
250-300	1.5450	0.9290	1.0805	0.316

Table 5: Physical properties of the different fractions of oil derived from the catalytic pyrolysis of used tyre (CaCO₃).

Temp. (°C)	η_{20}^D	D_{20} , gcm ⁻³	Refractivity Intercept (RI)	Refractive Index parameter (I)
i.b.-100	1.4350	0.6864	1.092	0.260
100-150	1.4648	0.7450	1.092	0.270
150-180	1.4675	0.7662	1.0844	0.280
180-200	1.4710	0.8234	1.0376	0.280
200-300	1.5010	0.8438	1.079	0.295

Table 6: Percentage (wt) of hydrocarbon group types in the oil derived from the catalytic pyrolysis of used tyre.

Hydrocarbon group	Oil derived with MgO	Oil derived with CaCO ₃
Aliphatic	25 %	25 %
Aromatic	55 %	50 %
Polar	20 %	25 %

Table 7: Percentage (wt) of phenols and carbonyls in the oil derived from the catalytic pyrolysis of used tyre.

	Oil derived with MgO	Oil derived with CaCO ₃
Phenols	1.86 %	1.47 %
Carbonyls	0.0178 %	0.0188 %

increase in refractive indices and densities with increasing boiling point of the fraction with both catalysts. At lower temperature low molecular weight hydrocarbons are present and with increase in boiling point the molecular weight of the compounds are also increased. Low values of refractive indices are associated with paraffins and higher values with aromatic hydrocarbons. The nature of the hydrocarbon group present in each fraction was further identified from the refractivity intercept (RI) and refractive index parameter (I). The beauty of these parameters is that it gives a specific value for each hydrocarbon group. The RI value of paraffins varies in the range of 1.048-1.05, naphthenes from 1.03-1.046 and aromatics from 1.07-1.105 [19].

The refractive index and RI of the fraction from initial boiling point to 100 °C of both oils show aromatic hydrocarbons of low boiling point. The chromatographic analysis indicates that 13.5 % and 16.5 % wt of low boiling point hydrocarbons are present in the first fraction using MgO and CaCO₃, respectively. The refractive index and RI of the oil fractions from 100-150° C also show aromatic hydrocarbons of relatively high boiling point with a 20 % wt with MgO catalyst and 25 % wt with CaCO₃ catalyst. Naphthenes are present in the fractions from 180-200 °C and 200-250 °C of oil using MgO catalyst with a total 41.5 % wt. The RI of both groups is in the range of 1.03-1.046. While the RI of the oil fraction from 180-200 °C of oil using CaCO₃ is near to RI value of paraffins with only 1 % wt of the total. The last fraction (~300 °C) in both oil samples is a mixture of hydrocarbons but with a higher wt (34 %) using CaCO₃ than MgO (11 %) catalyst.

Column chromatography

Separation of oil on silica gel column and analysis on GC were carried out with the aim to get an idea of the nature and type of compounds present in such oil. The sample was eluted with n-hexane for aliphatic, benzene for aromatic and methanol for polar hydrocarbons. Maximum number of hydrocarbons eluted with benzene both of low boiling point and high boiling point with 55 % wt and 50 % wt using MgO and CaCO₃ as catalyst, respectively (table 6). The major aromatic hydrocarbons are benzene and alkyl substituted benzene as confirmed by using standards. 25 % wt of aliphatic hydrocarbons present in both catalytically pyrolyzed oil samples. With

CaCO₃ catalyst the amount of polar compounds (25 % wt) in oil is greater than with MgO catalyst (20 % wt).

The oil derived from catalytic pyrolysis of waste tyre rubber are a mixture of aromatic and aliphatic compounds because the main component of automotive tyre is styrene-butadiene rubber (SBR), which has both aromatic structure (styrene-repetitive unit) and aliphatic structure (butadiene-repetitive unit). The presence of high amount of aromatic content is also due to the cyclization of olefin structures followed by dehydrogenation reactions and the Diels Alder reactions [6]. In the present study, it may be considered that formation of more aromatic hydrocarbons is due to the Diels Alder reactions during catalytic pyrolysis of tyre rubber.

Oxygenated compounds

Among the oxygenated compounds phenols and carbonyls were determined quantitatively in the polar fraction of the oil sample by spectrophotometric method which amount up to 1.86 % wt and 1.47 % wt for phenol and 0.0178 % wt and 0.0188 % wt sample for carbonyl of total oil sample with MgO and CaCO₃ catalysts, respectively (table 7). The presence of these compounds may be explained by the pyrolysis of oxygenated compounds of the tyre, such as stearic acid, extender oil etc. *Laresgati et al.* [7], *Pakdel and Roy* [20] also detected oxygenated compounds in tyre pyrolysis oils.

CONCLUSIONS

In this study, the conversion of used tyre into valuable liquid hydrocarbons was investigated. The effects of catalyst type and temperature on the product distribution and quality of oil from catalytic pyrolysis were investigated. The main conclusions are as follows:

1- Higher amount of oil was obtained with catalytic pyrolysis at 350 °C.

2- Fuel properties of oil from tyre pyrolysis with MgO and CaCO₃ catalysts were comparable with diesel fuel, except that higher amount of low boiling point hydrocarbons in the oil was derived with MgO catalyst (40 % gasoline fraction) as compared to oil was derived with CaCO₃ catalyst (10 % gasoline fraction).

3- Mixtures of hydrocarbons were present with higher concentration of aromatic hydrocarbons in both types of oil. The pyrolytic oil from MgO catalytic pyrolysis of waste tyre contained about 55 % aromatic hydrocarbons

whereas aromatic fraction in oil from CaCO₃ catalytic pyrolysis was 50 %.

Evaluation of waste tyre rubber using catalytic pyrolysis is very important from economic and environmental point of view as the gas and oil can be utilized and since as catalytic pyrolysis using solid bases as catalysts requires lower temperature.

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