Catalytic Pyrolysis of Waste Inner Rubber Tube into Fuel Oil Using Alumina and Calcium Carbonate Base Catalysts

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Summary: The waste inner rubber tube represents a source of energy and valuable hydrocarbons were catalytically pyrolysed in a batch reactor under atmospheric pressure. For this catalytic pyrolysis two economical base catalysts like Al_2O_3 and $CaCO_3$ were used. The effects of these two catalysts were determined in term of the yield of the derived gas, liquid oil, and solid char products. The liquid obtained from catalytic pyrolysis of waste inner rubber tube termed as parent oil was also refluxed with their respective catalyst for 2 hours. For the comparison both of the oil that is parent and refluxed oil were also characterized by physical and chemical tests. In case of using Al_2O_3 as a catalyst, the oil product containing higher concentration of polar hydrocarbons. As far as the distillation data and fuel tests are concerned, the oil fractions with both the catalysts fulfill the present specifications of diesel fuel commercial products.

Introduction

Butyl inner tubes are used as inner tubes and inner liners in tubeless tyres. After some time it is disposed as waste because its efficiency has become reduced. Proper disposal or beneficiation of waste inner butyl tubes are of the great concern, both environmentally and for resources conservation [1, 2]. There is an enormous potential for reclamation and reuse of butyl inner tubes. It can be used in many ways like damaged tubes can be patched. It can be also used for swimming aids and water containers. An important application of inner rubber tube is their use as fuel [3]. Recycling and reuse is the best option to achieve both these objectives and one form of recycling is pyrolysis. Nowadays rubber pyrolysis is at present an interesting and challenging area of research [4]. As compared to thermal pyrolysis, catalytic pyrolysis provides control of both the products quality as well as lowering the pyrolysis temperature [5-7]. This may lead to a high value hydrocarbon mixture which could reduce the required reaction temperature, improve the yield of products, provides selectivity in the product distributions and enhance the economic potential of the process [8, 9]. The use of catalysts in thermal pyrolysis of inner butyl tubes has been proposed as a way of producing high aromatic products for the production of gasoline and chemical feedstock [10-15].

The objective of the present study was to convert waste inner rubber tube catalytically at relatively low temperature into liquid hydrocarbons as well as to derive oil in the boiling range of commercial fuel oil. In the literature zeolites have been reported as a catalyst for catalytic pyrolysis of rubber tube but they are expensive [16-19]. In the present study two economical and easily available basic catalysts like Al_2O_3 and $CaCO_3$ were investigated to determine their influence on the yield and composition of the derived oil.

Results and Discussion

Yield of the Pyrolysis Products

The effect of temperature on the product distribution from pyrolysis of used inner rubber tube using alumina oxide and calcium carbonate catalysts are presented in Table-1. It can be seen from the results that product distributions of both catalysts changed significantly with increasing the temperature from 300 $^{\circ}$C to 400 $^{\circ}$C. The gas yield increased with increase in temperature but it is greater in case of using $CaCO_3$ catalyst as compared to Al_2O_3. The maximum yields of oil obtained at 350 $^{\circ}$C with both catalysts and further increase in temperature led to decrease in oil yield. For example, with Al_2O_3 catalyst the total gas yield rose from 25 to 30.97 mass % and oil yield fell from 40 to 34.52 mass % as the temperature of the pyrolysis was increased from 350 $^{\circ}$C to 400 $^{\circ}$C. When $CaCO_3$ was used as a catalyst the oil yield was lower and gas yield was higher compared to the Al_2O_3 catalyst Table-1. A

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temperature higher than 350 °C does not imply a conversion because the maximum possible conversion has already been achieved at this temperature.

The effect of amount of catalyst on the product distribution at optimum temperature is shown in Table-2. The results showed that in both of the cases catalysts the maximum amount of liquid oil obtained at 1 g (20%) of catalysts.

Similarly the effect of pyrolysis reaction time on the product distribution at optimum temperature and catalyst weight are shown in Table-3. The results show that in case of using alumina as a catalyst one and half hour is optimum time while in case of using calcium carbonate as a catalysts the maximum amount of liquid oil obtained in one hour.

Composition of Pyrolytic Oils

The pyrolytic oils obtained were characterized in terms of fuel characteristics those are shown in Table-4 and compared with the standard fuel values as given in Table-5. From the results it can be seen that density, API gravity, aniline point, diesel index of both catalytic pyrolysis lie in the range of kerosene. While refractive index lie in the range of diesel oil. Specific gravity, viscosity and kinametic viscosity values lie in the range of diesel. The flash point of oil using Al_2O_3 catalyst close to the flash point of kerosene fuel values but the flash point of oil using $CaCO_3$ as a catalyst is lower than that of diesel fuels but near to gasoline. The sulphur contents in both oils are close to the sulphur contents of diesel fuel. Therefore both types of pyrolytic oils can be used as fuel for combustion systems in industry.

Table-1: Effect of Temperature on product distribution from pyrolysis of used rubber tube.

Temp. °C	Al_2O_3 catalyst			$CaCO_3$ catalyst		
Reaction product, wt%	300	350	400	300	350	400
Gas	21.78±	25.0±	19.33±	30.73±	31.0±	33.0±
	0.424	1.80	0.31	0.230	0.20	1.17
Oil	21.68±	40.0±	34.52±	28.33±	30.27±	30.0±
	0.02	2.0	0.365	0.306	0. 306	0.20
Solid	56.54±	35.0±	34.5±	40.93±	38.73±	37.0±
	0.231	0.115	0.115	0.416	0.231	0.346

Table-2: Effect of catalyst on product distribution from pyrolysis of used rubber tube at 350 °C.

Reaction product, wt%	Al_2O_3 catalyst			$CaCO_3$ catalyst		
Of catalyst	Gas	Liquid	solid	Gas	liquid	solid
0.0	20.50±	16±	63.50±	22.25±	16.33±	61.45±
0.5	0.064	1.113	1.15	0.9157	1.160	0.9069
1.0	21.20±	22.67±	56.13±	27.0±	25.04±	47.96±
	0.600	0.702	0.1155	0.20	0.461	0.66.9
1.5	24.97±	40.20±	34.80±	31.0±	30.26±	38.74±
	1.13	0.529	1.226	0.20	0.02	0.18.
2.0	26.30±	39.00±	34.60±	40.27±	21.59±	38.14±
	0.416	0.3055	0.318	0.305	0.718	0.65
	27.13±	38.50±	34.37±	41.08±	21. 42±	37.5±
	0.305	0.100	0.251	0.04	0.225	0.011

Table-3: Effect of time on product distribution from pyrolysis of used rubber tube at optimum conditions

Reaction product, mass %	Al_2O_3 catalyst			$CaCO_3$ catalyst		
Time (hrs)	Gas	Liquid	solid	Gas	liquid	solid
0.5	6.5±	10.13±	83.37±	25.13±	23.91±	51.96±
	0.04	0.305	0.266	0.3055	0.416	0.274
1.0						
	25.0±	40. 0±	35.0±	31.0±	30.27±	38.73±
	0.20	2.00	1.800	0.20	0.115	0.305
1.5						
	25.5±	42.0±	32.5±	32.20±	29.93±	37.87±
	0.020	2.00	1.980	0.200	0.230	0.416
2.0						
	26.27±	41.90±	32.82±	34.27±	28.60±	37.13±
	0.305	0.0305	0.2772	0.305	0.400	0.011

Table-4: Fuel properties of pyrolytic oil obtained from catalytic pyrolysis of used tube rubber.

S. No.	Parameters	Oil derived with Al_2O_3	Oil Refluxed with Al_2O_3	Oil derived with $CaCO_3$	Oil Refluxed with $CaCO_3$	Oil Refluxed with MgO
1	Density (g/cm^3)	0.8116	0.821	0.787	0.783	0.7916
2	Specific gravity	0.817	0.821	0.792	0.7883	0.797
3	API gravity	41.695	40.851	47.14	48	46.06
4	Viscosity (Centipois)	3.249	3.347	1.372	1.209	1.371
6	Kinematic viscosity (mm^2/s)	4.003	4.078	1.744	1.545	1.732
7	Aniline point °C	60	58	59	62	59
8	Flash point °C	50	49	40	42	40
9	Watson characterization constant	11.325	11.367	11.635	12.15	11.60
10	Freezing point °C	-12	-11	-16	-15	-16
11	Refractive index	1.454	1.466	1.450	1.456	1.455
12	Diesel index	57.19	55.72	65.147	68.93	63.655
13	% Sulfur	38	37	60	60	60
14	Bromine number	46.35	46.32	43.53	43.45	43.46
15	Phenols	1.46%	1.86%	1.67%	1.74%	1.77%
16	Carbonyls	0.0170%	0.0168%	0.0188%	0.0178%	0.0182%

Table-5: Standard parameters of gasoline, diesel and kerosene oil.

S. No.	Parameters	Gasoline	Diesel	Kerosene
1	Density (g/mL)	0.736/0.725	0.834	0.780-0.82
2	Specific Gravity	0.70	0.85	0.78
3	API gravity	65	23-30	41.7-39.66
4	Viscosity (Centipois)	0.7750-0.8394	2.0-4.5	0.9-1.5
5	Kinematic viscosity (mm^2/s)	5.0	3.77 -5.0	2.2
6	Aniline point °C	65	71	62
7	Flash point °C	37.8-38	55-60	50-55
8	Watson characterization constant	12.45	11.28	12.126
9	Freezing point °C	-58	-54	-
10	Diesel index	83.44	54	59.88
11	Bromine number	60	1-10	
12	Gross calorific value (MJ/kg)	45.6	43.5-55.7	46.5
13	Sulfur %	1ppm	0.70ppm	0.9ppm
S.No	ASTM Distillation	Temp °C	Temp °C	Temp °C
0	Dew point	49	120	110
1	10 mL	69	225	178
2	20mL	78	238	180
3	30mL	82	252	180
4	40mL	86	272	182
5	50mL	90	281	190
6	60mL	94	290	192
7	70mL	98	299	198
8	80mL	102	300	200
9	90mL	106	301	210
10	100mL	112	305	220

ASTM Distillation

Hydrocarbon groups generally found in rubber tube derived pyrolytic oil fractions are paraffinic, naphthenic, aromatic and olefinic. The quality and characteristics of rubber tube 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 quality of pyrolytic oil. The hydrocarbon groups of the oil derived from catalytic pyrolysis of rubber tube are in the boiling range of 80-217 °C for using Al_2O_3 as a catalyst while in case of using $CaCO_3$ catalysts are in the boiling range of 70-259 °C, respectively.

Column Chromatography

Separation of oil on silica gel column was 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 60 % mass and 55 % mass using Al_2O_3 and $CaCO_3$ as catalysts respectively. Those results are given in Table-6 (Fig. 1). The major aromatic hydrocarbons are benzene and alkyl substituted benzene as confirmed by using standards.

Table-6: Percentage of hydrocarbon group in the oil derived from the catalytic pyrolysis of used rubber tube

Hydrocarbon Group	Oil derived with Al_2O_3	Oil derived with $CaCO_3$
Aliphatic	25%	25%
Aromatic	60%	55%
Polar	15%	20%

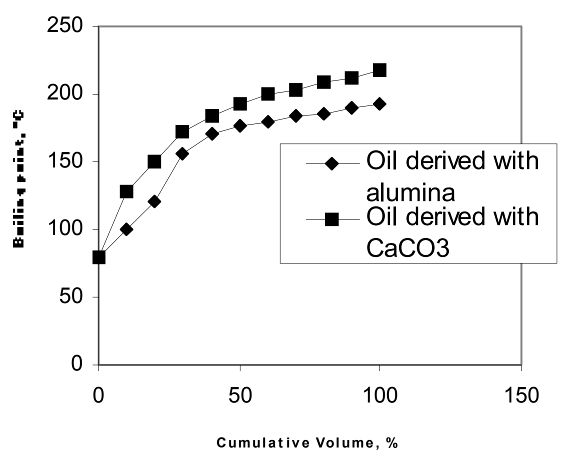


Fig. 1: ASTM distillation curves of oils derived from catalytic pyrolysis of waste rubber tube at 350 °C.

Oxygenated Compounds

Among the oxygenated compounds such as phenols and carbonyls were determined quantitatively in the polar fraction of the oil sample by spectrophotometric method using folins dennis and 2,4-dinitrophenylhydrazine reagents which amount up to 1.46 % mass and 1.43 % mass for phenol and 0.0157 % mass and 0.0164 % mass sample for carbonyl in the oil samples respectively. The presence of these compounds may be explained by the pyrolysis of oxygenated compounds of the rubber tube such as stearic acid, extender oil etc.

Experimental

Material and Methods

The sample was produced from waste inner rubber tube of 5-10 mm wide pieces. The pyrolysis experiments were carried out in a batch reactor under atmospheric pressure. A fixed amount of waste inner rubber tube sample and catalysts of 1g was loaded in a reactor and heated. The gaseous products passed through a trap, where the liquid hydrocarbons were collected.

Liquid and solid products of pyrolysis processes were determined for each experiment by weighing the amount of each product obtained and calculating the corresponding percentage using the formula as given below. The gas yield was determined by difference.

$$\% \text{ Conversion} = \frac{\text{Wt. of rubber} - \text{Wt. of residue}}{\text{Wt. of rubber}} \times 100$$

$$\% \text{ Oil} = \frac{\text{Wt. of oil}}{\text{Wt. of rubber}} \times 100$$

$$\% \text{ Residue} = \frac{\text{Wt. of residue}}{\text{Wt. of rubber}} \times 100$$

$$\% \text{ Gas} = \% \text{ Conversion} - (\% \text{ Oil} + \% \text{ Residue})$$

where Wt. = Weight

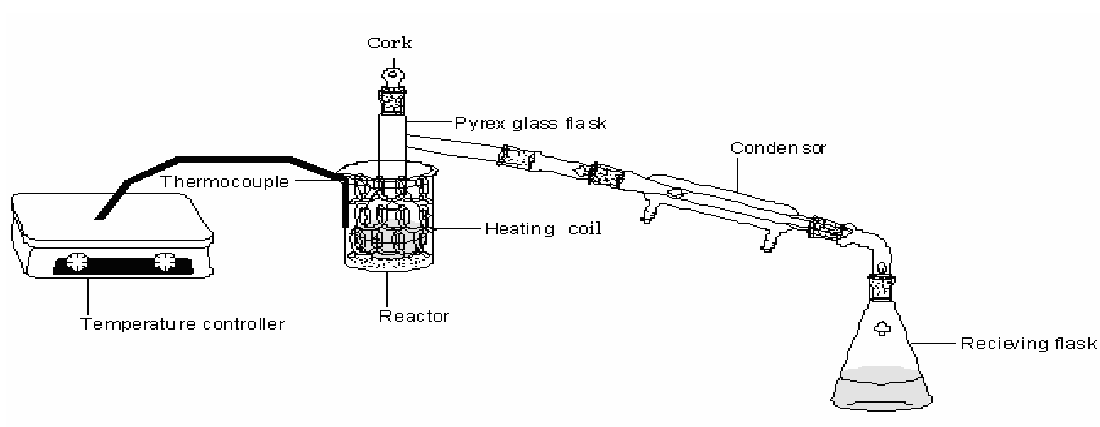
Determination of Physiochemical Properties of the Liquid Product

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 oil. The silica gel 60 (63-200 μm grain size, supplied by Merck) was packed into borosilicate glass column and the pyrolysis oil 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 oil, respectively.

Fractional distillation was carried out to separate different boiling point hydrocarbon fractions from the liquid derived from catalytic pyrolysis of waste inner rubber tube. The oil was distilled at a specific temperature until no more distilled products were collected.

Some physical properties of pyrolytic oils were determined by using the following standard methods: Flash point 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, Kinametic 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.



Batch Reactor Assembly

Conclusion

In this study the conversion of used rubber tube 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. Catalytic pyrolysis with Al_2O_3 gave higher oil product and less amount of gas.
2. Fuel properties of oil from rubber tube pyrolysis by using Al_2O_3 and $CaCO_3$ catalysts were similar, except the flash point of oil derived with Al_2O_3 catalyst was higher than the oil derived with $CaCO_3$.
3. Mixtures of hydrocarbons were present with higher concentration of aromatic hydrocarbons in both types of oil. The pyrolytic oil from Al_2O_3 catalytic pyrolysis of used rubber tube contained about 60% aromatic hydrocarbons whereas aromatic fraction in oil from $CaCO_3$ catalytic pyrolysis was 55%.
4. It can be concluded that the oil derived from catalytic pyrolysis can be blended with the kerosene, gasoline and diesel fuels.

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