Conversion of Low Density Polyethylene into Fuel Products Using Indian Fuller's Earth as Catalyst

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Summary: The catalytic activity of Indian Fuller,s earth was explored for the cracking of polyethylene. The catalyst was used both in the crude and activated form. The catalytic activity of these was discussed in terms of the structure and composition of the catalyst. The yields of reactions were determined by the relative amounts of oil, wax and gas produced during the process. The amount of catalyst, temperature of prolysis and time for reaction was optimized during this investigation. The yields of the reactions were found to have boiling point in the range of 300 °C. The distillation data of oil showed that about 15% have the boiling range of light naphtha 35% of the heavy naphtha and 60 % of the middle distillate. The liquid and gaseous products can be used as fuel while the wax can be considered as feed stock for the petroleum industry. The liquid and wax products were separated by G.C. equipped with F.I.D. The liquid and wax products were analyzed using the IR spectroscopy. These were found to contain olefin, paraffin and aromatic hydrocarbons.

Introduction

Plastic waste has been increased alarmingly in the last many years. This is because of its wide use and the non-biodegradable nature. Among the plastics polyethylene, polypropylene and polystyrene are of the wide spread use. The use of low density polyethylene is far greater than others specifically in the third world countries. It is widely used as shopping bags in addition to other uses, therefore contribute greater to the plastic waste. This waste is a real threat to the environment because it is a petrochemical product whereas its incineration is expensive which may loss of renewable carbon resource. The best option is its conversion into useful products. Its thermal cracking converts it into fuel products or feed stock for the oil industry [1-6]. About 10% of the energy of waste is used for the conversion of waste plastic into useful product [7]. Nevertheless, thermal cracking of plastic may produce large number of olefins and it is also very much non-selective [8]. The use of catalyst narrows the range of products [7] and some times eliminates olefins. The catalysts used for the thermal cracking of plastics include zeolites, oxides, and sulfides [9-13]. Some workers also used treated clays or clays for the conversion of waste plastics into useful products [14-15]. The use of solid acid catalyst for the cracking of plastics is also reported [16].

In the present work Indian Fuller's earth also known as Multan clay was used as catalyst for the cracking of polyethylene into oil and gas products. Indian fuller's earth is bentonite clay and is rich in magnesium oxide. The idea behind this work is to use low cost and products selective catalyst that also lowers the cracking temperature and reaction time. Since clays are mixtures of silicates, oxides and ion exchangers, therefore the synergistic effect of these will be exploited for product selective lower temperature cracking of polyethylene. This work is part of the work on the investigation of the catalytic activities of clays for the cracking of plastics. The reactivity of Indian Fuller's earth /Multan clay was found different from already investigated both the Gachi and China clays due to the difference in chemical composition.

Mechanisim of the Catalytic Activity of Clays

The catalytic activity of the clays can be explained on the basis of the composition of clays.

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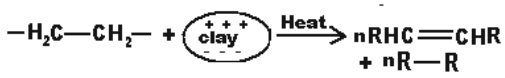
Clays are composed of silicates and various quantities of the oxides of metals. These compounds offer static charge and vacant orbital in addition to charged holes and macro porous and meso porous structure. At high temperature these sites become more prominent due to the changes in vibrational energies. These cationic and anionic sites induce charge into the polyethylene molecule. This results in the imbalance of the molecular charge cloud which destabilizes the polyethylene molecule and consequences cracking. In addition to this cracking secondary and tertiary cracking of the thermal and catalytic nature are also expected, therefore a variety of products are formed during this process.



Results and Discussion

Indian Fuller's earth or Multan clay was found an effective catalyst for the cracking of polyethylene into fuel products. The catalyst was used, both, in the crude and activated form. The idea behind the use of catalyst in these forms was to investigate the effects of the structure and composition of the catalyst on the product distribution and the yield and rate of the reaction. It was observed that catalytic activity of Indian Fuller's earth is improving the nature of resulting products. The products contain aromatics in addition to olefins and paraffin hydrocarbons. However, the previously investigated Gachi clay was found to contain only olefin. The large quantities of unwanted olefin are due to the chance of conversion into polyolefin. The presence of aromatics in the products can be correlated to the chemical composition of the catalyst which contains greater quantities of the magnesium oxide which is basic in nature. The cracking efficiency of the Indian Fuller's earth / Multan clay is greater than that of the Gachi clay. This can be determined from the greater quantities of the wax products. This is due to the effective cracking of plastics by the macro porous structure of the clay.

The product of pyrolysis was found to contain wax and liquid fractions in addition to gases. Liquid and wax fractions were obtained quantitatively while the concentration of gases was investigated by taking difference. The relative amount of products was found to depend upon the mass of catalyst and temperature for the reaction. It can be seen from the graph that the mass of wax is more than liquid both for higher concentration as well as lower concentrations of catalyst. Series 1 of the graph represent the liquid while 2 is for the wax product. In case of large quantities of catalyst most of the plastic molecules are in direct contact with it, therefore, converted into high molecular weight compounds and escapes away. In case of the lower concentrations there is slow interaction with catalyst which lowers the amount of liquid product. The cracking efficiency is the same for all concentrations of catalyst which was based on the amount of residue and remains same for all the ratios. The residue is a mixture of plastic additives and char in case of the completion of reaction and for incomplete reactions it is a mixture of unreacted plastic, char and plastic additives. Based on the higher concentration of liquid product 3:1 ratio was selected as the optimum ratio for the reaction. This study was conducted for the crude form of Indian Fuller's Earth/Multan clay. Further investigations both for the crude form of catalyst and activated one were carried out using 3:1 ratio.

The progress of reaction and the relative amount of the liquid, wax and gaseous products also depend upon the temperature. It can be seen from Table-1 that the amount of residue decreases with increase in temperature and the amount of the residue comes to a constant level at 300 °C. It is observed that the amount of wax product is less than the higher temperature therefore it was selected as the optimum for reaction. Table-1 also contains results for the activated Indian Fuller's Earth/Multan clay. It was observed that the catalytic activity of the activated form is greater than its hydrated form which can be seen from Table-1 in terms of percentage of the residue at various temperatures. Time optimization

Table-1: Investigation of the optimum temperature for maximum conversion of polyethylene.

	Multan Clay (Hydrated)				Multan Clay (Activated)			
Temperature (°C)	Liquid (%)	Wax (%)	Gas (%)	Residue (%)	Liquid (%)	Wax (%)	Gas (%)	Residue (%)
200	24.20 ± 0.09	1.00 ± 0.07	9.8 ± 0.06	65.00 ± 0.04	47.55 ± 0.05	------	10.25 ± 0.05	42.20 ± 0.05
250	45.50 ± 0.09	2.50 ± 0.08	7.00 ± 0.00	45.00 ± 0.08	76.00 ± 0.05	6.50 ± 0.05	5.30 ± 0.05	12.20 ± 0.04
300	58.33 ± 0.04	36.60 ± 0.05	2.9 ± 0.00	2.2.00 ± 0.05	32.60 ± 0.05	62.50 ± 0.05	4.90 ± 0.05	2.20 ± 0.05
350	47.50 ± 0.08	42.50 ± 0.05	8.00 ± 0.05	2.20 ± 0.05	25.80 ± 0.06	68.5 ± 0.08	2.6 ± 0.05	3.00 ± 0.05
400	38.60 ± 0.08	48.70 ± 0.05	10.00 ± 0.05	2.20 ± 0.05	29.00 ± 0.04	66.3 ± 0.09	1.70 ± 0.05	3.00 ± 0.05

studies were also investigated and it was observed that at optimum conditions of temperature and catalyst the reaction with activated clay catalyzed reaction was faster. The reaction catalyzed by activated clay completed with in 15 minutes, however, in case of hydrated clay, it was slow and completion of reaction took place in approximately 30 minutes (Figure-1). This difference in reactivity is due to the difference in crystalline structure and composition of the clay. In case of activated clay the catalyst have more active sites which enhance the cracking process and produce the greater quantities of wax. However, in case of the hydrated clay the reaction is slower and produces high boiling point compounds which remain in the reaction vessel and pass through further cracking. The resulting compounds have lower boiling point and lower molecular weight. Therefore, the hydrated clay catalyzed reactions give larger quantity of the liquid product.

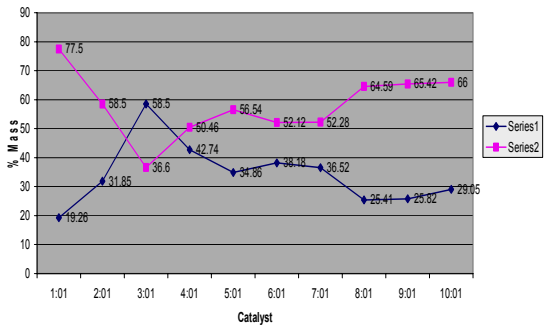


Fig. 1: Optimization of Catalyst.

Experimental

Material and Methods

Waste but clean samples of low density polyethylene were used as raw material, while the Indian Fuller's Earth or Multan clay was used as catalyst. Multan clay is bentonite clay, the crude form is named as the hydrated Multan clay and thermally treated form is known as the activated Multan clay. Activated Multan clay was prepared by heating the hydrated clay at 700 °C for 3 h in a furnace. On cooling, it was passed through sieve of 100 µm mesh for uniform particle size. Both, the activated and hydrated Multan clay were used as catalyst for the conversion of waste polyethylene into useful products .The conditions for the reaction were optimized for the hydrated clay and the reactions for activated clay were also carried out under these conditions. The sample and catalyst were mixed in 3: 1 ratio and the mixture was placed in a glass reactor of 58 mm internal diameter and 350 mm length. The glass reactor was placed in an externally heated furnace connected to the thermocouple. The mixture was heated for half an hour in the pre-heated furnace. The products of pyrolysis *i.e.* liquid and wax were received in cold traps on distillation and the gases were allowed to escape.

Analysis of the Product

All the liquid and wax samples were analyzed and separated by Carlo Erba gas chromatograph equipped with flame ionization detector. Separation was carried out by 6x22 MT metal column packed with OV 1. The injector and detector temperatures were 350 °C and 240 °C, respectively. The column temperature was programmed at the rate of 5 °C per minute from 40 to 300 °C. Solutions (1%) of the liquid and wax products of pyrolysis were prepared in chloroform, separately and 6µl each of these solutions were used for the gas chromatographic analysis. It was observed that the composition of both liquid and wax fractions is similar except the relative concentration of the components. The liquid products were found to contain greater concentration of the low boiling point components and the wax was found to contain higher concentrations of the high boiling point compounds. In the chromatograms some smaller peaks were also observed many of which were unresolved. In case of the activated clay catalyzed reactions the number of these unresolved peaks was higher. However, the number and position of the major components was the same for both type of the catalysts. The number of major components was found the same in liquid and wax samples for both the reactions. The nature of liquid and wax products was found the same for both the crude clay and activated clay catalyzed reactions.

Distillation Analysis

The oil obtained at the optimum conditions was distilled under atmospheric pressure. It was observed that about 15% of the oil distills at the range of 160 °C which is the boiling point limit of the light naphtha, about 35% of the oil was obtained as distillate in the boiling point range of 160-205 °C which corresponds to heavy naphtha and about 50% of the oil was found the middle distillate (220-300 °C). This data indicate that the oil obtained during this

process the kerosene and diesel range of petroleum products.

Infra Red Spectral Analysis

All the liquid and wax products were identified using infrared spectroscopy. The absorption was measured in the range of 400-4400 cm^{-1}. It was observed that both the liquid and wax are broad spectrum mixtures containing aliphatic, olefinic and aromatic hydrocarbons. The spectra for all the samples were found to contain the same positions of the peaks which were appeared at 1411, 1643,2854,2950,3000 and 3100 cm^{-1}. These peaks are characteristic of the parafinic, olifinic and aromatic hydrocarbons.

Conclusion

The catalytic activity of Indian Fuller's earth/Multan clay for the cracking of polyethylene was investigated and it clay was found an effective catalyst for the cracking of polyethylene. The rate of reaction and relative concentration of the liquid and wax product were depending upon the nature, composition and crystalline structure of the catalyst therefore the nature of products is different from the reaction catalyzed by other clays. Further the rate of reaction for activated Indian Fuller's earth/Multan Clay catalyzed reaction is greater than hydrated clay and the amount of wax product for the activated clay catalyzed reaction is also higher than the hydrated clay. The chemical composition of both the liquid and wax products was found the same which was determined from the I.R. and gas chromatographic analysis. Both, the liquid and wax was found to contain aliphatic and aromatic hydrocarbons. The only difference between the liquid and wax is in the relative proportion of low and high boiling point compounds.

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