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Conversion Of Waste PVC Into Liquid Fuel

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Abstract: Polyvinyl chloride (PVC) is rated second only after poly ethylene (PE) as volume leader in the plastic industry. Waste PVC poses serious environmental problem because of its high chlorine content (56%) and non-biodegradable nature. Treatment of waste PVC by incineration or pyrolysis produces toxic chloro emissions which adversely affect environment, ecology and human health. Catalytic degradation of PVC was performed using a fluidized bed reactor with catalyst such as Fe_2O_3, ZSM-5, Pd/$A\ell_2O_3$ in the temperature range 100 – 430°C. Arrangement was made to adsorb liberated chlorine on $CaCO_3$. The effect of feed to catalyst ratio and temperature were evaluated for the maximum liquid yield. Maximum liquid yield of 12.17% was obtained using catalyst ZSM-5 at 3:1 feed to catalyst ratio.

Keywords: Polyvinyl Chloride; Recycling; Degradation; Catalysts; Fuel

1. Introduction

Plastics are generally non-biodegradable, so the continuous increase in plastic production and consumption lead to accumulation of high amounts of polymer waste which pose serious environmental problems.[1] Therefore, various methods for recycling of waste plastics have been developed, among which "chemical recycling" is most promising technique. This technique treats waste polymer to recover valuable products [1,10]. Pyrolysis process consists of thermal decomposition of waste plastic at moderate temperatures and total absence or in presence of low amount of oxygen in which the structure of polymer breaks down into smaller hydrocarbons. [6] There is an abundance of literature on the recovery of fuel through pyrolysis of waste plastic.[12,15] Due to versatility of polyvinyl chloride (PVC) in terms of application, its global demand exceeds 25 million tons per year. Table -1 shows predicated post consumer PVC composition from year 2000 to 2020[9]: The main problem during the recycling of waste PVC is its chlorine content. Thermal degradation of PVC leads to the production of chloro-organic compounds and when it is moderately heated, PVC polymer produces toxic and corrosive hydrogen chloride (HCℓ) [3,9]. It is necessary to remove chloro-organic compounds while producing fuel from PVC.

Table -1: *Predicted (2000–2020) post-consumer PVC waste composition [9]*

Source	PVC waste (kg ton/year)				
	2000	2005	2010	2015	2020
Automobile	528	562	580	627	645
Electrical/Electronic	323	384	452	537	589
Household/Commercial	938	1097	1314	1670	2088
Packaging	599	525	519	569	624
Construction	1132	1377	1676	2061	2399
Others	60	60	60	62	62

Basically dechlorination can be divided into three groups: stepwise pyrolysis, catalytic pyrolysis and pyrolysis with adsorbent added to the sample. It is reported that in a stepwise pyrolysis of PVC, the maximum Cℓ content was released from PVC at 300°C [4,9,13]. In catalytic pyrolysis, some metal containing catalysts inhibits the formation of HCℓ. Finally, HCℓ is removed by using adsorbents like $CaCO_3$, CaO, $Ca(OH)_2$, Na_2CO_3, $NaHCO_3$ since the evolved HCℓ is trapped by means of physical and/or chemical adsorption and retained in the solid fraction [9, 13]. The role of metal catalysts in PVC recycling is shown in figure -1 [9]

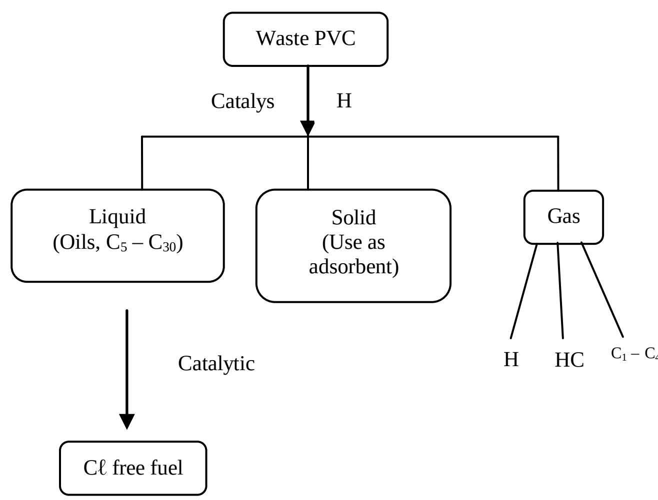

Figure -1: *Catalytic Recycling of PVC [9]*

In the present work efforts have been made to decompose PVC using catalyst Fe_2O_3, ZSM-5, Pd/$A\ell_2O_3$ to get maximum liquid yield with different feed to catalyst ratio at various temperatures.

2. Material and Methods

2.1 Materials

Raw material PVC (collected from a Municipal Solid Waste (MSW) Site Jodhpur, Rajasthan) was thermally cracked in the presence of various catalysts in inert atmosphere. PVC material collected from the source was washed in water to remove dust and dirt material. PVC particles of ≤2mm were

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prepared by cutting and shredding. PVC particles were mixed with $CaCO_3$ (purity >98.5%). The purpose of mixing the feed with $CaCO_3$ was essentially to trap HCℓ liberated due to cracking of PVC [13]. The different catalyst Fe_2O_3, ZSM-5, Pd/$Aℓ_2O_3$ was used in the experiment.

2.2 Experimental Setup

In this study semi batch fluidized bed reactor was used. As shown in the figure -2, feed mixture of PVC and $CaCO_3$ in appropriate ratio was placed on the bed – I and catalyst was placed on bed – II. Catalyst was continuously fluidized with inert gas N_2 coming from the bottom of the reactor. Reactor was heated with a heating coil. After attaining the softening point, the liquid droplets of PVC started dropping from bed – I and came in contact with particle of fluidized bed. After cracking, the gaseous product was condensed and collected in the vessel. The cracking temperature range was varied from 300 – 430°C. In the second set of experiments the position of feed and catalyst was interchanged, meaning there by that the lower bed was raw material and catalyst on the upper bed. In this situation the vapor stroke gases moved upwards and contacted catalyst. This procedure did not give any advantage in terms of quality and quantity of liquid product, probably because of thermal cracking prior to catalytic cracking.

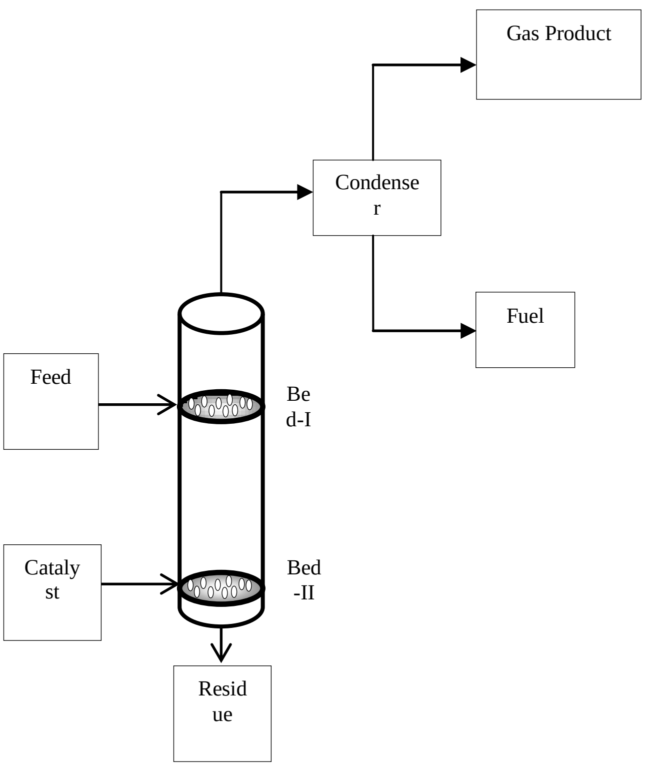

Figure -2: *Diagram showing position of Feed and Catalysts in the Reactor*

3. Observations

Experiments were carried out by using different feed to catalyst ratio as given in table -2:

Table -2: *Quantities of Feed and Catalysts*

Feed to Catalyst ratio	Quantity (g)	
	Feed	Catalyst
1:1	200	200
2:1	267	133
3:1	300	100
4:1	320	80

In all the experiments total weight of feed and catalyst together was kept 400g. The catalyst used was Fe_2O_3, ZSM-5, Pd/$Aℓ_2O_3$. As reported in the literature [13] feed material was heated and maintained at 300°C for 30 – 60 minutes in order to liberate HCℓ. The amount of $CaCO_3$ used corresponds to an stoichiometric relation Ca:Cℓ of 3:1, which has been proposed by author [13]. These gases adsorbed and reacted with $CaCO_3$ present there as per reaction shown below:

$$CaCO_3 + 2HCℓ \rightarrow CaCℓ_2 + CO_2 + H_2O$$

The liquid yield obtained was very insignificant up to 300°C due to very little catalytic cracking of PVC. At this temperature it was essentially dehydrochlorination. After dehydrochlorination process at ~300°C, temperature was raised to obtain maximum liquid yield of desired quality using different feed to catalyst ratio by varying temperature in the range of 300 - 430°C.

4. Results and Discussion

The liquid yield obtained using different feed to catalyst ratio (1:1 to 4:1) using catalyst namely Fe_2O_3, ZSM-5, Pd/$Aℓ_2O_3$ are shown in fig 3 to 5:

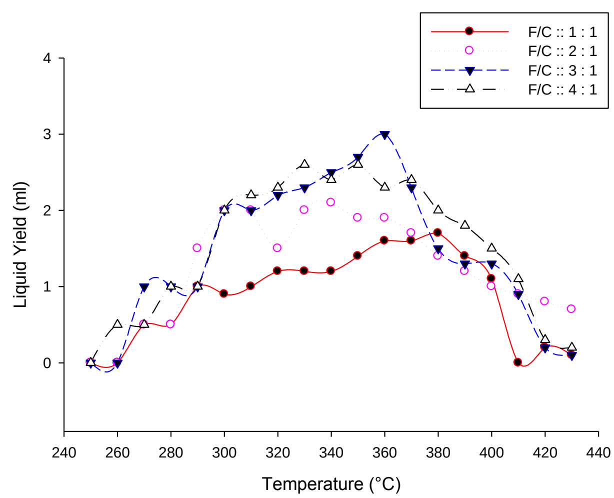

Figure 3: *Effect of variation of feed (PVC) to catalyst ratio on liquid yield with Catalyst Fe_2O_3*

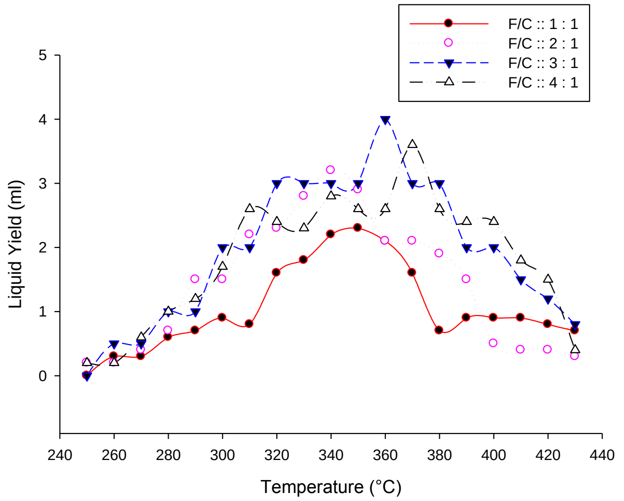

Figure 4: *Effect of variation of feed (PVC) to catalyst ratio on liquid yield with Catalyst ZSM-5*

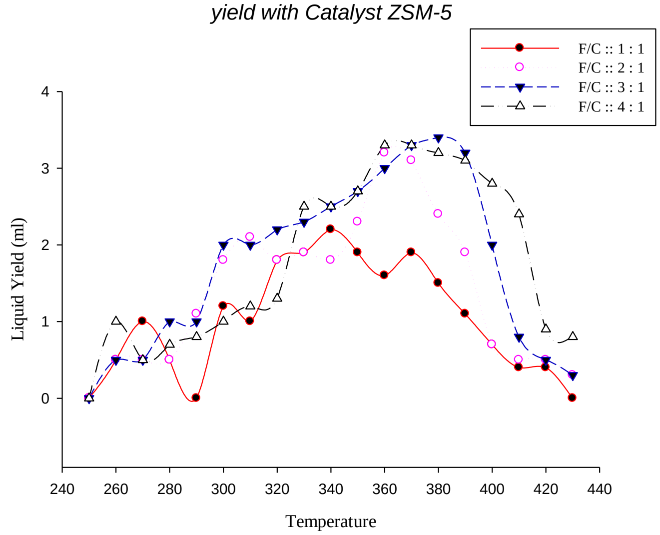

Figure 5: *Effect of variation of feed (PVC) to catalyst ratio on liquid yield with Catalyst Pd/Aℓ$_2$O$_3$*

From these figures it can be seen that for the given feed to catalyst ratio, initially liquid yield increases with increasing temperature, on further increase in temperature maximum yield was obtained in the temperature range 300 - 380°C. Further increase in temperature reduces liquid yield possibly because of severe cracking and beyond 480°C cracked product was non-condensable gases.

Table -3: *Percentage liquid yield obtained from PVC cracking with different Catalysts*

F/C Ratio	Total Liquid Yield (%)		
	Fe_2O_3	ZSM-5	Pd/Aℓ$_2$O$_3$
1:1	8.30%	10.05%	9.80%
2:1	8.84%	10.15%	10.07%
3:1	9.10%	12.17%	11.07%
4:1	9.00%	10.91%	10.63%

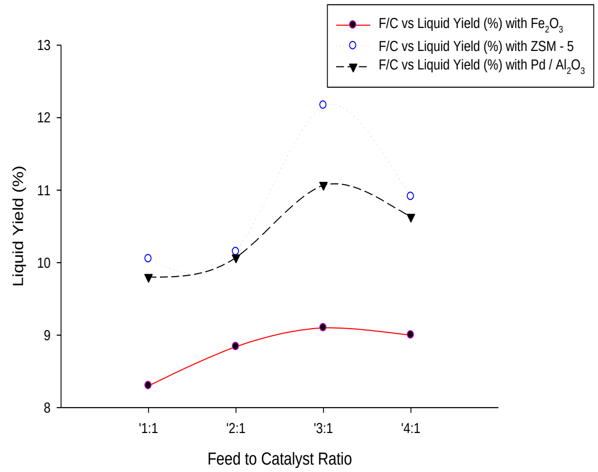

Figure 6: *Liquid yield (%) from PVC with different Feed to Catalyst Ratio*

It can be observed from Table -3 and Figure 6 that as feed to catalyst ratio increases from 1:1 to 3:1 the total product liquid yield increases. Further increase in feed to catalyst ratio from 3:1 to 4:1 liquid yield drops down. With catalyst ZSM-5 total yield increases from 10.05% to 12.17% thereafter it drops down from 12.17% to 10.91%. Using Fe_2O_3 and Pd/Aℓ$_2$O$_3$ the yield increases through ratio 1:1 to 3:1 and remains almost constant. Maximum liquid yield was obtained with 3:1 feed to catalyst ratio, which was 9.1%, 12.17% and 11.07% for catalyst Fe_2O_3, ZSM-5, Pd/Aℓ$_2$O$_3$ respectively. It seems that the lower yield obtained using catalyst Fe_2O_3 is more likely due to catalyst Fe_2O_3 becomes active at temperature more than 600°C. Pd catalysts suffer from deactivation with time-on-stream; this may be due to coke deposition, formation of surface metal halides and metal sintering, perhaps this is the reason for obtaining comparatively lesser liquid yield with catalyst ZSM-5.

5. Conclusion

Among the various catalysts studied, maximum liquid yield of 12.17% was obtained using catalyst ZSM-5 and feed to catalyst ratio 3:1. The optimum temperature range for PVC catalytic cracking was 350 – 380°C. It has been proved that the application of various catalysts and different feed to catalyst ratio plays a significant role on the quantity of pyrolysis liquids. $CaCO_3$ adsorbent was efficient enough to adsorb chlorine present in the gases. There was no liquid yield below 200°C and above 480°C the product was essentially non-condensable. Hence by this method waste PVC can be converted into fuel, which will not only solve the problem of its disposal but also give a valuable product for the society.

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