



Characterization of Liquid Products Obtained from Catalytic Co-Cracking of Polypropylene Waste and Residual Fuel Oil

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The characterization of the liquid produced from the co-cracking of Polypropylene extrusion grade (PPX) and Residual fuel oil (RFO) was carried out using analysis techniques like Gel Permeation chromatography (GPC), Ultimate analysis, Calorimetry analysis, Fourier-transform infrared spectroscopy (FTIR) analysis and Nuclear magnetic resonance (NMR) analysis technique. The resulting liquid from the co-cracking of the two feedstocks in presence of catalyst Zeolite Socony Mobil-5 (ZSM-5) was observed to have high calorific values of 44.084 MJ/Kg comparable to that of the commercial diesel and therefore has the potential to be used as source of renewable fuel. The temperature and catalyst have been found to have positive synergistic effect on the heating value of the liquid product. GPC analysis has revealed that, the liquid obtained from RFO is quite complex, but the complexity is reduced by co-cracking with PPX as suggested by the reduction in the polydispersity index, while the NMR analysis shows that the liquid obtained from the co-cracking was more of aliphatic in nature. The FTIR spectrum obtained from the co-cracking of RFO and PPX both in the presence and absence of catalyst was observed to be a mixed spectrum of their individual component and addition of catalyst had an insignificant effect on the properties of the resulting liquid except in the calorific values which were increased. The spectrum shows that the liquid product was dominated by the presence of alkanes and alkenes.

Keywords: Catalyst, Pyrolysis, Residual fuel oil, Spectra, ZSM-5

Introduction

Exponential growth in the plastic industry sector has contributed in the waste generation and as a result the importance of plastics in our livelihood is overshadowed by its negative impact on the environment. Besides government norms, practical approaches including mechanical and chemical recycling are required¹, recycling can also reduce resources going to landfill sites² while the pyrolytic process may be another approach in line with environmental sustainability.³ The use of biomass energy sources for harvesting electricity and other types of energy has also been explored⁴, cracking of biomass like rice husk to obtained gas energy.⁵ Further, the pyrolysis of mixed waste plastics have been explored and found that it affects one another during the pyrolysis reaction.⁶ Pyrolysis of single plastics through simulation⁷⁻¹⁰ has been used by many researchers to advance the investigation on the execution of pyrolysis process. Computer aided simulation has also been used to simulate the pyrolysis of waste lubricant oil⁸ and analysis of the performance.

Co-pyrolysis of waste plastics with waste lubricant oil was carried out producing a diesel like fuel was carried out in recent times.¹¹ Various analytical techniques like the Gel Permeation Chromatography (GPC) was employed to study and understand the weight distribution of molecules (MWD) of the polymer used in the experiment.¹² The degradation process of oil shale kerogen and its pyrolysis behaviour was studied using Thermogravimetric Analysis- Fourier-transform infrared spectroscopy (TGA-FTIR)¹³, while FTIR analysis technique has been used to spot the functional groups in an organic and inorganic compound.¹⁴ Most of the previous work has focused on the used lubricant oil, co-cracking with municipal plastics waste. However, the residual fuel oil which is one of the low valued residues of the refineries has not been co-cracked with specific waste plastics to investigate on the possibilities of upgrading to lighter fuel oil or more valued products. While RFO are piling up in the refineries, plastic wastes especially packaging plastic wastes has entered every space including water ways, ocean and landfills creating a disaster like future for our environment. Therefore, it is imperative to choose this material and consider for possible damage control while recovering the waste through environmentally

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friendly methods, while simultaneously creating an alternate path of energy source through chemical recycling route of pyrolysis.

The aim of this work is to analyse and characterize the liquid oil product resulting from the co-cracking of RFO with polypropylene waste in a batch reactor, using various analysing technique like to understand the MWD, calorific values, elemental content, of the liquid product resulting from the cracking of the mixtures and the individual polymers in the presence of ZSM-5 catalyst in order to pave way for further investigation envisage its applications. The relevance and novelty of this work are that, this characterisation can reveal in-depth properties of the liquid product and would therefore help in optimization the process including variable parameters, substantiated by the analysis, thereby opening a new scope of improvement to realise a value-added product from the process.

Experimental

Material

Polypropylene polymer (PP) extrusion grade (PPX) used in the moulding of disposable cups collected from industry and Residual Fuel Oils (RFO) collected from Indian Oil Corporation Limited, Guwahati, while Zeolite Socony Mobil-5 (ZSM-5) with mole ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$) of 30:1 in the catalytic pyrolysis was used in our experiment. The characteristics, the source of these materials and the process of the experiment are reported elsewhere.¹⁵

Methods

Gel Permeation Chromatography (GPC) analysis was carried out using Chloroform as the solvent, SIL-20A autosampler, Shim-pack XR Series columns with its micro-plunger design, the LC-20AD with solvent-delivery system. During the operation the oven temperature of 40°C and pressure of 72 kg/cm², with

Pump Flow: 1 ml/min maintained during the analysis was used to understand the molecular weight distribution of the liquid products obtained through co-pyrolysis of residual fuel oil with plastics. Further, FTIR (make NICOLET of USA; model IMPACT 410) was employed to determine the functional groups in the product. Bomb calorimeter with 1108 P oxygen bomb and 6775 digital thermometer (make: Parr Instrument Co. USA, model: Catalogue No. 13341EE, with working principle Isoperibol, time controlled and dynamic system) was used to analyse the calorific values of the samples. While CHNS (O) Analyzer (Make: Thermo Finnegan, Italy, Model series of FLASH EA 1112) was used in order to establish the percentages of Nitrogen, Hydrogen, Carbon, and Sulphur based on the principle of "Dumas method" which oxidises the sample completely and instantaneously by "flash combustion".

Results and Discussion

GPC analysis

The molecular weight distributions of the liquid product resulting from the co-cracking of PPX with RFO are shown in Table 1. The maximum of the liquid product (55%) was found to possess, number average (Mn) and weight average molecular weight (Mw) of 71 and 111 respectively with a polydispersity of 1.57. Around 44% of the liquid was found to possess Mn of 17 and Mw of 21 with a polydispersity of 1.21. The polydispersity as shown in Table 1 is a reflection of the divergence in the molecular weight distribution from the ideal compound as per Gaussian distribution, the broader range of the compounds present in the sample is indicated by the higher polydispersity.

The liquid product from RFO was found to possess Mn and Mw of 90 and 206 respectively and the

Table 1 — Molecular weight distribution of liquid products obtained from the co-cracking of RFO and PPX

SL No. Sample	OBSERVATION							
	Molecular weight %	(Mn)	(Mw)	(Mz)	(Mz+1)	Polydispersity	Remark	
1 PPX	55.153	71	111	219	405	1.573	catalyst ZSM-5 was used in all cases	
	44.052	17	21	24	26	1.217		
	0.723	3	3	3	3	1.020		
	0.070	1	1	1	1	1.018		
2 RFO	100	90	206	409	715	2.286		
3 RFO/PPX	81.564	67	124	507	2418	1.849		
	18.435	17	19	20	21	1.080		
Mn	Number Average Molecular Weight			Mw	Weight Average Molecular Weight			
Mz	Average Molecular Weight			Mz+1	Average Molecular Weight			
Mw/Mn	Polydispersity							

polydispersity index was observed to be 2.28. However, from the co-cracking of RFO and PPX, most of the liquid product (81.56%) showed a Mn of 67 and Mw of 124 with a polydispersity of 1.84, while 18.43% showed a Mn and Mw of 17 and 19 respectively with a polydispersity of 1. The polydispersity of liquid RFO shows that the liquid obtained is quite complex, indicating that the sample contain a broader range of complex compounds.¹⁶ The data shows that the Mn of RFO+PPX derived liquid is more like that of the PPX-derived liquids. Moreover, we observed that there are overall decrease in the distribution of molecular weight of the liquid products when RFO and PPX are co-process together, in addition, decrease in the polydispersity index of co-cracked liquid from that of the individual RFO and PPX was observed. This implies that the decomposed product of PPX during the process can further react with the pyrolysis product of RFO there by facilitating the co-cracking reaction. Further, the polydispersity index of the liquid obtained from the co-cracking of the RFO and PPX was reduced compared with the average theoretical values of their individuals, reflecting a synergistic effect in the co-cracking reaction.

FTIR Analysis

The FTIR analysis is one of the important techniques to identify different functional groups' characteristic that may be present in the feedstocks and product resulting from the pyrolysis. Upon interaction of the pyrolysis oil with infrared light the chemical bond will elongate and contract and as such infrared radiation will be absorbed in a specific range of wavelength even if the other portion of the molecular structure may be different. The FTIR spectra for the liquid fuel products resulting from the optimized condition of thermal and catalytic pyrolysis of RFO and PPX is presented in Fig. 1.

The FTIR spectra of liquid acquired from the thermal and catalytic cracking of PPX as in Fig. 1(a) showed almost a similar spectra, showing a medium broadband at 3422 cm^{-1} which may be an indication of presence of hydroxyl group as the band between 3345–3880 cm^{-1} substantiate the existence of hydroxyl groups (O-H, C-O-O-H stretch).¹⁷ The addition of additive during the processing of the polymer may be responsible for the detection of hydroxyl groups in the spectra of Polypropylene.¹⁸ Panta and Singh¹⁹ reported that PP has a higher inclination to oxidation among the polymeric

materials due to the existence of the tertiary carbon which is bonded to the methyl group which can easily form peroxide in the chemical form of (-C-O-O-H) if oxygen is present even at low temperature which further decomposes to more stable compounds like carbonyl (-C=O), hydroxyl (-O-H), and Nitro (-N=O) groups. Functional groups like amine (C-N, N-H) with wave band at 1159 cm^{-1} for both thermal and catalytic pyrolytic oil and 1654 cm^{-1} for the thermally

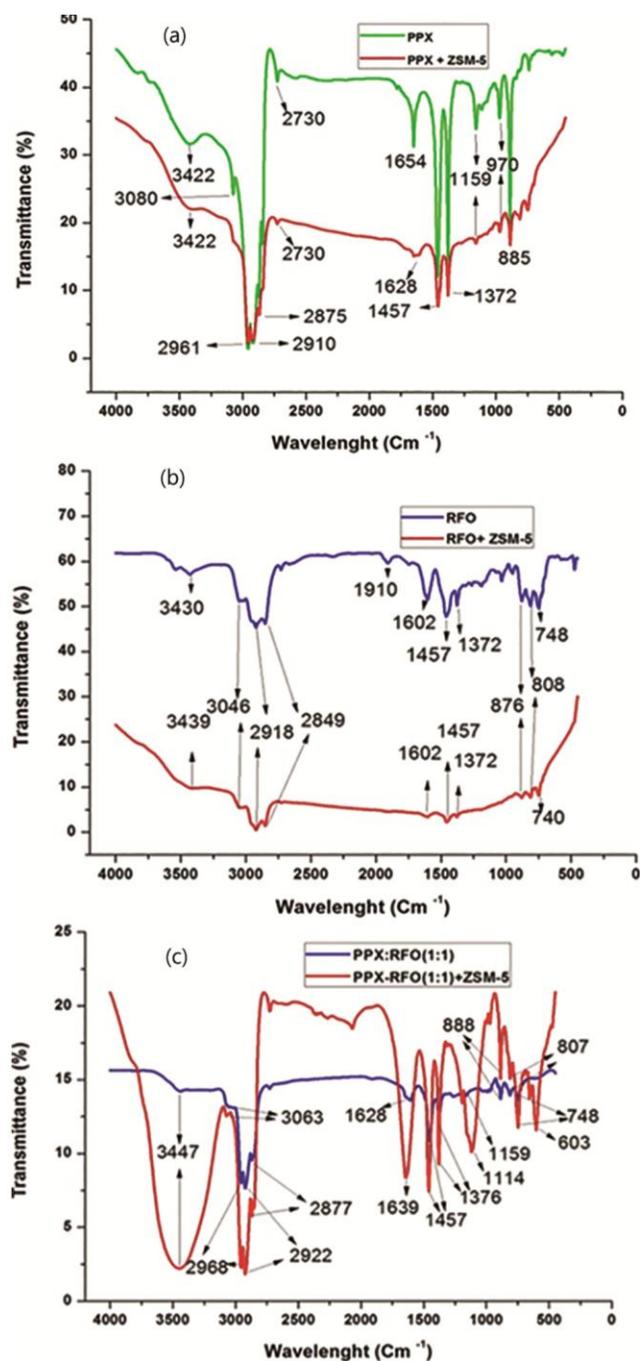


Fig. 1 — FTIR spectrum of RFO, PPX & RFO & PPX

cracked oil product were also observed, a similar report was found by Hakeem and team.¹⁰ However another indication of a peak at 1654 cm^{-1} which is within (1640–1680 cm^{-1}) confirms the presence of alkene for the thermally cracked oil of PPX and 1628 cm^{-1} for the catalytic oil products which is in the range of (1660–1600 cm^{-1}) confirms C=C stretch, it was reported similarly by Ahmaruzzaman.¹⁶ But, the band at 1457 cm^{-1} shows that aromatic rings (C=C) wavelength.¹⁷ However, the presence of alkanes is also noticed by C-H bending and scissoring vibration at 1457–1453 cm^{-1} , which verifies the presence of benzene derivatives in the pyrolysis oil. Moreover, CH bending vibration at 990–966 cm^{-1} indicates the existence of alkenes.²⁰ And the band at the 1372 cm^{-1} may be due to alkene (-CH₃-) bending vibration²¹, and in both the spectra, the peak at 885 cm^{-1} observed between 890–886 cm^{-1} band validates the occurrence of vinylidene functional group in the composition of the product.²⁰ The peak at 3080 cm^{-1} may be²¹ due to H bonded NH which may be from material PP which contains <0.30 trace of Nitrogen (ASTM D 5291.a).²² And the presence of a band at wavelength 2910 cm^{-1} shows that the alkanes CH stretching vibration are present.²⁰ And spectrum 2875 cm^{-1} may be due to the aliphatic hydrogen (C-H stretching vibration)²³ resulting from the symmetric -CH₃- and 2861 cm^{-1} may be from the asymmetric Methylene group -CH₂ which²⁴ occurs at 3000–2850 cm^{-1} range.

The FTIR analysis spectra of the liquid yield resulting from the catalytic cracking of RFO Fig. 1(b) and the original feed closely resemble each other with slide shifts from the other. The presence of O-H group in the spectra was indicated by the peak at 3439 cm^{-1} and C-H stretching vibration of C-CH₃ is detected at 3046, 2918 and 2849 cm^{-1} while the peak at 1602 cm^{-1} indicates an aromatic ring stretching but could not find the confirmation peak of the C=C absorption peak at 1652 and 1675 cm^{-1} .⁽¹⁶⁾ The presence of alkane is detected by C-H scissoring and bending

vibration at 1457 cm^{-1} similar result was found by Pramendra.¹⁴ The peak at around 1372 cm^{-1} may be S=O compound and peaks at 876 and 808 cm^{-1} may be due to di-substituted and tri-substituted alkenes respectively. The peak at 740 cm^{-1} may be indicative of C-H cyclic deformation, which suggests either aromatic or more likely -CH₂ which has split because of interaction in the long molecular chain because usually aromatic C=C bending occurs in the band between 650–750 cm^{-1} .

The FTIR spectra of the pyrolytic oil from co-cracking of PPX+RFO both in the presence and absence of catalyst ZSM-5 essentially consist of mixed spectra from each component as shown in Fig. 1(c). The broad peak at 3447 cm^{-1} is an indication of the presence of the hydrogen-bonded -OH groups. While the spectra at 3063 cm^{-1} may be a suggestion of the presence of sp² C-H bending, the sp³ stretching vibration that was indicated by the band between 3000–2800 cm^{-1} and confirmed by the C-H Stretch peaks at 1457 cm^{-1} and 1376 cm^{-1} . The peak at around 2800–2700 cm^{-1} may be an indication of the C-H stretching of aldehyde. And the peak at 1639 cm^{-1} in the spectra of PPX+RFO+ZSM-5 confirms the presence of olefinic compounds.²⁵ The peaks between 1260–1000 cm^{-1} indicate the presence of C-O stretch vibration of alcohol, while the peaks at 888 cm^{-1} closely resemble that of the spectra obtained for the individual components indicating the presence of vinylidene functional group. The peaks at 807 and 737 cm^{-1} which was also present in the spectra of RFO suggest the presence of the substituted alkenes and even phenyl ring substitution bands which were observed by Pramendra.²⁰

Ultimate Analysis and Bomb Calorimetry

The result of ultimate analysis as shown in Table 2 is an indication of the appropriateness of the feedstocks for the pyrolysis process in accordance with its high carbon percent value recorded. The occurrence of Nitrogen (N) in the PPX may be because

Table 2 — Ultimate and calorific value analysis of liquid from individual cracking and catalytic (ZSM-5) co-cracking of RFO and PPX

Sample & Temperature →		PPX	RFO	RFO+PPX	RFO + PPX+ ZSM-5	PPX + RFO + ZSM-5
Particular ↓						
Test	Composition %	500°C	500°C	500°C	500°C	600°C
Ultimate analysis (Liquid)	Carbon (C)	85.936	87.624	88.601	86.83	87.926
	Hydrogen (H)	9.539	8.781	8.952	10.582	7.790
	Nitrogen (N)	1.925	2.074	1.684	1.672	2.080
	Oxygen (O)*	2.60	1.521	0.763	0.916	2.204
Calorific Value (Liquid) MJ/Kg →		43.638	41.972	42.112	44.084	42.709

• By difference

of the additives used during the processing of the polymers. While the Nitrogen present in the RFO may be traced back to its origin crude oil in addition to the additives used in petroleum products and consequently resulting in the occurrence of nitrogen in the liquid product of RFO+PPX. Oxygen is calculated by difference, assuming that the whole of the fuel is composed only of C, H, N and O since sulfur was not detected, which may be due to its negligible content in the solution. The deviation in the properties of RFO is expected since it depends on the crude oil source and the extent of refinery processing received by the fuel oil blending component or additives. The variation in the percentage of elements observed in the various liquid products are reported in Table 2, clearly indicates that co-cracking between the feedstock, temperature, and addition of catalyst has an impact on the outcome of the process and hence its degree of characteristics.

The calorific value which defines the energy released when a unit mass of fuel is burned in the presence of sufficient air is one of the important properties of fuel which indicates the efficiency of the fuel. The calorific values of the liquid product obtained from the co-cracking of PPX and RFO and their individuals are given in Table 2. It is observed that the expected average theoretical value of calorific values when PPX and RFO were co-cracked together was found to be 42.112 MJ/Kg at the processing temperature 500°C in the absence of the catalyst. But, there is a significant augmentation in the calorific values by addition of catalyst at the same temperature recording a calorific value of 44.084 MJ/Kg, which is very close to the calorific values of Diesel which has 44.94 MJ/Kg.²⁹ However, under similar conditions, except increasing the temperature to 600°C, the calorific value was found to be 42.7091 MJ/Kg. This suggests that the co-cracking of PPX and RFO gave rise to a reaction resulting in a synergistic effect which is also influenced by the temperature and catalyst used in the process.

Conclusions

The weight distribution of molecules suggested that the products from the pyrolytic degradation of PPX can react with the pyrolysis product of RFO thereby assisting the co-cracking reaction, and as a result, the synergistic effect was observed. The molecular weight distribution of liquid products from co-cracking of PPX and RFO was more like that of PPX derived liquids. While the FTIR spectrum of the liquid

products acquired from the thermal and catalytic co-cracking of RFO+PPX was essentially found to be a mixed spectrum of their individual component and more closely resembles the spectra of the PPX. Moreover, the liquid products are observed to have greater presence of alkane and alkene compounds. Ultimate analysis suggests that the source of the feedstock, process temperature and presence of catalyst results in the variation of percentage of the element present in the final product. GPC analysis shows that the polydispersity of the co-cracked liquid was lower than that of the individual RFO, implying a reduction in the complexity in the nature of the compound and synergistic interaction between the two in the process of cracking.

The addition of catalyst in the process has been found to enhance the fuel characteristics especially in the calorific value of the liquid product at the lower temperature of 500°C. The calorific values of liquid products from RFO+PPX+ZSM-5 co-cracked at 500°C were found to be 44.084 MJ/Kg which is very similar to that of the diesel fuel. This implied that co-cracking of PPX with RFO both of which are low graded, least value material and available in abundance can be upgraded to higher value products and can therefore, be a potential renewable energy source.

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