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Catalytic Pyrolysis of Waste Mixed Plastic to Useful Hydrocarbons

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Abstract- Thermal pyrolysis of waste plastic in an autoclave, leads to the formation of multiple products viz. hydrocarbon gas, liquid distillates and solid coke products, via thermal cracking route. Various metal additives have been evaluated during waste plastic pyrolysis experiments conducted under N2, at different temperatures and varying reaction time, in an autoclave. We present a detailed report on the conversion of mixed plastic (LD) waste to useful liquid and gas hydrocarbon products via pyrolysis route. The effect of various metal catalyst additives on the pyrolysis yield and distribution is elucidated.

Keywords- *Pyrolysis, Mixed Plastic Waste, Metal Catalysts*

I. INTRODUCTION

In the recent years, the dramatic supply of low-cost plastic to fulfill high demand in various applications such as packaging, single use containers and long term applications viz. textile, construction materials, transportation and electronics, has resulted into the accumulation of waste plastic, a global problem with serious environmental ramification. Currently, global production of plastics is approximately 350 million tons/year; with production forecasted to triple by 2050, accounting for around 20% of global oil consumption. The chemical industry has been developing a variety of recycling opportunities with the goal to eventually achieve a circular economy for sustainable plastics consumption. Mechanical recycling of plastic waste is the predominant method of recycling practiced today. In mechanical recycling, the polymer is not broken down, but remains intact and is formulated to lower value plastic products. Incineration, is another method that is used to convert waste plastic into heat and electricity; however it is not an energy efficient recycling process due to heavy energy loss.

For the longer term, thermal pyrolysis of plastic waste is the only means of attaining a complete circular economy of plastic waste. In thermal pyrolysis, the plastic is heated in an inert atmosphere at high temperatures to break down the polymer into lower molecular weight products that can be used as feedstock for chemical plants and for fuel, reducing the reliance on crude oil. A major challenge in this process is the capital cost and energy requirements of thermal pyrolysis plants. A free-standing pyrolysis plant will reduce quantity of plastic waste but may have difficulty in delivering reductions in net energy consumption or net carbon emissions.

Plastics like polypropylene (PP) or low density mixed plastics (mixed LD) can be pyrolyzed in an autoclave to produce useful chemical feedstock or fuel hydrocarbon products. Polypropylene (PP) and low density polyethylene (LDPE) yield about 70 percent fuel yield1. An added advantage of conducting the pyrolysis in an autoclave is that we can isolate the metal content in plastic waste, which after the conversion process is complete, remains behind in the char that also contains glass, calcium carbonate, clay and carbon black contaminant additive1. Thermal pyrolysis of plastics can be conducted in an autoclave that operates at high temperature, i.e. 500°C and above which is an ideal temperature for plastic decomposition.

II. LITERATURE REVIEW

Various catalyst additives have been reported in earlier literature in the conversion of waste plastic to useful products. Miandad R. et al reported catalytic pyrolysis of waste plastics (PS, PE, PP, and PET; single or mixtures in different ratios), in the presence of modified natural zeolite (NZ) catalysts, modified by thermal activation at 550°C and acid activated with HNO3, to enhance its catalytic properties. They found that in presence of the modified catalysts, highest liquid distillate yield (60-70%) was obtained for polystyrene (PS) pyrolysis as compared to PP or PE pyrolysis (40-50%)2. Miskolczi Investigated the pyrolysis of real waste plastics (high-density polyethylene and polypropylene) in a pilot scale horizontal tube reactor at 520 °C temperature in the presence and absence of ZSM-5 catalyst. He reported that yields of gases, gasoline and light oil could be increased in the presence of catalyst and that the plastic wastes could be converted into gasoline and light oil with yields of 20–48% and 17–36% respectively depending on the experimental conditions3. Suhartano et al reported the pyrolysis of plastic waste (HDPE and LDPE) over natural zeolite at 480°C, pyrolysis in presence of catalyst yielded a fuel oil product whose physical properties and FT-IR characteristics closely resembled those of kerosene fuel4.

Trisunaryanti et al have reported hydrocracking of LDPE plastic at 350°C into gasoline fuel (>70%) over supported reduced bi-functional catalysts prepared by loading Ni, Ni-Mo, Co and Co-Mo active metal on the mordenite crystalline type natural zeolite5. P. Dwivedi et al have presented an overview of polymeric waste management towards sustainable environment and has elucidated the effect of various parameters on pyrolysis in the presence of catalyst additives6. R. Miandad et al have explained the characteristic effects of various catalysts on polymer pyrolysis process7. Catalysts influence the mechanism and kinetics of polymer pyrolysis and play a vital role in improving the quality of product distribution as well as optimizing the process parameters8, 9. L. Quesada et al have reported that catalysts may direct the selective formation of various products during waste plastic (LDPE film waste) pyrolysis at 500°C and thereby choice of catalyst is very crucial in determining the final product distribution. From experimental results, the authors concluded that zeolite-Y and zeolite-β favor the formation of smaller amount of waxes than catalysts viz. FCC, ZSM-5 or SnCl210. N. Mishra et al. have presented recycling of waste polypropylene plastics bags to high petroleum fuel oil (>90%) over nanoform nickel catalyst at 550°C11. Y. Al-Douri et al reported the comparative pyrolysis of PP and LDPE using catalysts comprising 2 metal oxides (Fe, Ni, Fe2O3, NiO) and 3-metal nanoparticles (Fe and Ni) as a catalysts supported on feldspar clay. Liquid distillate formed over nano-catalysts was found to possess much better properties than those for liquid distillate product obtained over metal oxide catalysts12. H. W. Lee et al have reported the catalytic pyrolysis of PE and PP over two types of mesoporous catalysts, desilicated Beta (DeBeta) and Al-MSU-F (AMF). The authors highlighted the effect of difference in catalyst acidity and mesopore size on the pyrolysis temperatures of waste plastics and pyrolysis products' distribution13. M. Al-asadi et al. have reported the pyrolysis of waste PET using Ni-ZSM-5, Ni-y-zeolite, Ni-β-zeolite and Ni-natural zeolite (clinoptilolite) at temperatures between 600 – 900°C in a horizontal tubular reactor. The authors reported that increase in temperature and nature of catalyst direct an increase in gas yields and that the pyrolysis oil yield decreased with increasing temperature 14. T. U. Han et al reported the pyrolysis of 2 types of Tetra Pak material, a type of aluminum–Kraft paper–plastic laminate used as packaging material for beverages and liquid food. Pyrolysis was performed over acidic catalysts viz. HZSM-5 (SiO2/Al2O3 = 30), H-Beta (SiO2/Al2O3 = 38), and Al-MCM-41(SiO2/Al2O3 = 20). 15. A. K. Panda et al have reported pyrolysis of waste PP, LDPE, HDPE and a mixture of all three over sulfated zirconium hydroxide catalyst between 400 – 550°C, to yield >79% oil, containing C10–C24 hydrocarbons16. Waste plastic pyrolysis has been reported over classical Lewis acids, such as AlCl3, FeCl3, TiCl4 and TiCl3, fused metal tetrachloroaluminates [M(AlCl4)n] where (M = Li, Na, K, Mg, Ca or Ba and n = 1 or 2)17.

We report herein, an economic, environmentally friendly and sustainable catalytic pyrolysis route to eliminate plastic waste. The role of various catalyst additives viz. metal naphthanate and octoate salts, metal sulfides and supported metal catalysts in the formation of useful products during pyrolysis of waste plastic viz. low density mixed plastic (mixed LD) in an SS-316 autoclave has been investigated. We also present the possibility of tailoring of pyrolysis products' distribution (in terms of upgraded distillate products and suppressed coke formation) in the autoclave, by selection of suitable catalyst additives.

III. METHODOLOGY

Low density mixed plastics waste (mixed LD) has been procured locally. A typical batch reaction comprises a charge of mixed LD chips feedstock (60 - 80g) and catalyst additives (dosages in terms of varying active metal content) taken in the SS-316 autoclave. The catalyst additives investigated during this study include Ca, Na, Fe and Mg naphthenates, Zn, Ce and Cu octoates, Zn oxide and Zn sulfide and γ-alumina supported ruthenium and copper oxide catalysts. The reaction temperature within the autoclave is maintained between 360 - 400°C, 430°C and >455°C, during the reactions. The reactions have been performed for 1, 2 and 4h in the presence of the catalyst additives and product distribution of liquid, gas and solid (coke) fractions has been reported. The transfer tube that allows for the passage of volatile lower boiling products (<370°C) into the adjacent collectors (for liquid products) and gas fractions' collectors is maintained at 245°C. Gas collector pressures is always maintained at around 3bar. Stirring of 200rpm has been maintained for all reactions. Post reaction, the reactor has been allowed to cool down to 140°C and then opened. Post pyrolysis the products comprise, a clear liquid distillate, a dark liquid residue, gas fraction and solid coke. The liquid distillate in the collectors is weighed and analysed by Pyr-GC/MS. Gas component is weighed but not qualitatively analyzed.

III. RESULTS AND DISCUSSION

To establish base line conditions, the waste mixed LD plastic is exposed to autoclave conditions, separately, in the absence of catalyst additives. The pyrolysis of waste mixed LD has been investigated between 4 temperatures viz. between 360 - 400°C, 430°C and >455°C, in the presence and absence of catalyst additives. The active content of catalyst additives has also been varied. Reactions were carried out from 1, 2 and 4h, respectively. Data for the product distribution (%) profiles at the different reaction temperatures (°C), run time (h) and varying catalyst active content (ppm) have been presented in Tables 1-6.

Mixed LD pyrolysis runs over metal octoate and naphthenate catalyst additives at >455°C:

Data for product distribution (%) for the mixed LD pyrolysis in the autoclave at >455°C are presented in Table 1.

At >455°C, after 4h, there occurs formation of clear liquid distillate, coke and gas fractions as reaction products. Typically, the runs are characterised by a high liquid distillate product fraction (between 83 - 85%; runs 1 - 4). Blank run (Run 1) in absence of catalyst additives shows a product distribution comprising 83.8% liquid distillate, 1.3% coke and 14.9% gas. From the different octoates and naphthanetes used, Lower dosages of Zn octoate appears to be the most efficient catalyst additive at >455°C for upgrading the liquid distillate yield.

TABLE I. MIXED LD PYROLYSIS RUNS AT >455°C, OVER METAL OCTOATE AND NAPHTHENATE CATALYST ADDITIVES (VARYING ACTIVE CONTENT) AT 4H RUN TIME

No	PE (g)	Catal.	Catal. (ppm)	T (h)	Prod. Distr. (%)			
					A	B	C	D
1	80	Nil	NA	4	83.8	0	1.3	14.9
2	60	Zn octoate	9.8	4	84.7	0	0.85	14.4
3	60		32	4	83.3	0	1.2	15.6
4	60	Na naph	32	4	82.2	0	1.9	15.9

A = clear liquid distillate; B = dark liquid residue; C= Coke; D= Gas

Furthermore, when lower dosages of Zn octoate (9.8ppm active Zn; Run 2) are used , the liquid distillate fraction is increased to 84.7% (9.8ppm active Zn; Run 2) as compared to blank (83.8%), at the same time coke formation is significantly suppressed to 0.85% as compared to blank run (1.3%). However in the presence of higher dosages of metal octoate and / or naphthenate catalyst additives (Run 3; Zn octoate, 32ppm active Zn and Run 4; Na naphthenate, 32ppm active Na), there is a reduction in the liquid distillate fraction as compared to blank with an increase in coke formation. Coke formation is highest for high dosages (32ppm active Na; Run 4; 1.9%) of Na naphthenate catalyst additive. Higher dosages of Zn octoate and Na naphthenate catalysts (32ppm active Zn and Na metal) facilitate increased formation of gaseous product fraction (Zn octoate (15.6%); Na naphthenate (15.9%), as compared to either blank (14.9%) or at lowered dosages of Zn octoate, indicating that the further decomposition of the waste mixed LD substrate is promoted by Zn octoate and Na naphthenate at higher dosages. Hence we can conclude that at >455°C and 4h run time, in order to upgrade the liquid distillate fraction, lower dosage of Zn octoate catalyst additive (9.8ppm active Zn) is the catalyst of choice and if we wish to upgrade the gaseous fraction, then higher dosages (32ppm) of either Zn octoate or Na naphthenate may be used as catalyst additive.

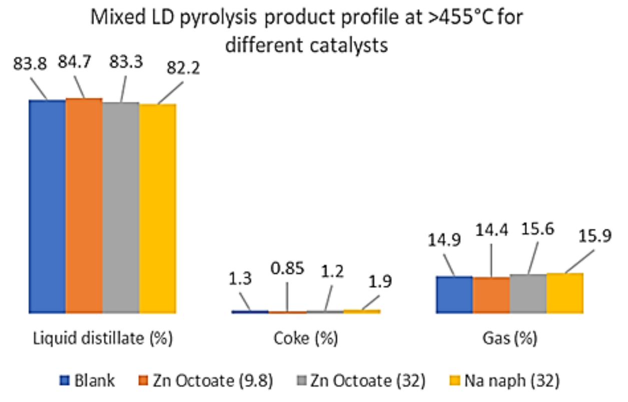

Figure 1. Effect of metal octoate and naphthenate catalyst additives on product distribution (%) at around 430°C:

Data for product distribution (%) for the mixed LD pyrolysis in the autoclave at reaction temperature around 430°C are presented in Table 2.

TABLE II. MIXED LD PYROLYSIS PRODUCT DISTRIBUTION (%) AT AROUND 430°C, OVER METAL OCTOATE AND NAPHTHENATE CATALYST ADDITIVES AT VARYING ACTIVE CONTENT AND AT DIFFERENT REACTION TIME

No	PE (g)	Catal.	Catal. (ppm)	T (h)	Prod. Distr. (%)			
					A	B	C	D
5	60	Nil	NA	4	73	12.3	0	14.7
8	60	Zn octoate	32	4	75.1	10.1	0	14.9
9	60		64	4	75.4	10.5	0	14.1
6	60	Nil	NA	2	70.2	15.9	0	13.9
10	60	Zn octoate	9.8	2	70.2	15.5	0	14.3
11	60		32	2	71.5	14.4	0	14.1
12	60		64	2	71.9	13.6	0	14.6
13	60		94	2	71.0	14.6	0	14.4
14	60		125	2	70.4	15.6	0	14.0
7	60	Nil	NA	1	62.3	23.1	0	14.6
15	60	Zn octoate	9.8	1	62.1	23.6	0	14.3
16	60		32	1	62.4	23.7	0	13.9
17	60		64	1	63.2	23.5	0	13.3
18	60		94	1	62.0	24.6	0	13.4
19	60		125	1	61.9	25.1	0	13.0

A = clear liquid distillate; B = dark liquid residue; C= Coke; D= Gas

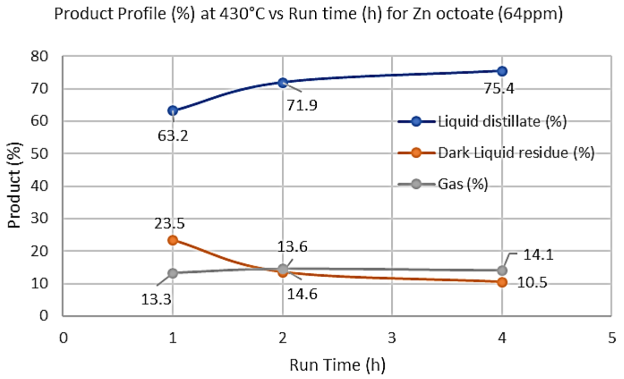

Figure 2. Reactions over Zn octoate catalyst additives at around 430°C

Catalytic pyrolysis runs have been conducted with Zn octoate with varying active Zn content and reaction times viz. 1, 2 and 4h and results summarized in Table 2 (runs 5 to 19). From the data presented in Table 2, when Zn octoate is used as the catalyst additive, there is formation of clear liquid distillate, dark liquid residue and gas fractions as reaction products. Coke is not observed from 1 to 4h run time. Blank run conducted for 1h, (Run 7) shows a product distribution comprising 62.3% liquid distillate, 23.1% dark liquid residue and 14.6% gas. At increasing active Zn doses, product distribution profile after 1h run time is characterised by a liquid distillate product fraction (between 61 – around 63%), dark liquid residue (between 23 – around 25%) and gaseous product (between 13 – 14%) (Runs 15 – 19). At 430°C, in presence of increasing dosages of Zn octoate at 1h run time, a gradual lowering of clear liquid distillate content with a simultaneous increase in the dark liquid residue and decrease in the gas component is observed. In 1h run time 430°C, highest liquid distillate formation is observed for Zn octoate (64ppm active Zn content). Fig. 2 shows the effect of run time (h) on product distribution (%) for Zn octoate (32ppm).

As the run time is increased from 1h to 2h, there is a considerable comparative change in the product distribution profile (compare runs 15 – 19 at 1h run time with Runs 10 – 14 at 2h run time). From the data presented in Table 2, in the presence of Zn octoate as catalyst additive and at 430°C, 2h run time, here also there is formation of clear liquid distillate, dark liquid residue and gas fractions. Coke is not observed at 2h run time. Blank run conducted for 2h, in the absence of Zn octoate catalyst additive (Run 6) shows a product distribution comprising 70.2% liquid distillate, 15.9% dark liquid residue and 13.9% gas. This indicates reaction time is an important factor affecting the product distribution. At 430°C, on increasing the run time from 1h to 2h, a dramatic increase in the liquid distillate accompanied by lowering of dark liquid residue content is observed, whereas the gas component distribution at 2h run time is closely identical to that at 1h run time. The runs conducted at constant 2h reaction time and varying active Zn content are characterised by a liquid fraction (between 70 – 72%), dark liquid residue (between 13 – ~15%) and gaseous product (~14%) (Runs 10 – 14). For increasing dosages of Zn octoate (from 9.8 to 64ppm active Zn content), there is increase in clear liquid distillate fraction and gas fraction to a maximum of 71.9% and 14.6% respectively. Further increase in active zinc content from 98 to 125ppm, leads to decrease in both liquid fraction and gas content, whereas dark liquid residue content is increased. This indicates that higher dosages of Zn octoate catalyst additive promote the formation of the dark liquid residue instead of the clear liquid distillate. At 430°C and 2h run time, active zinc content of 64ppm is optimum dosage to achieve higher liquid and gases fraction while keeping the dark liquid residue to minimum.

As the run time is further increased from 2h to 4h, increase in liquid fraction content while suppressing the dark liquid residue and no formation of coke is observed (Runs 8 – 9 at 4h run time). From the data presented in Table 2, in the presence of Zn octoate as catalyst additive and at 430°C, 4h run time, formation of clear liquid distillate, dark liquid residue and gas fractions is observed. Coke is not observed at 4h run time. Blank run (Run 5) conducted for 4h, shows a product distribution comprising 73% liquid distillate, 12.3% dark liquid residue and 14.7% gas. Product distribution profile for runs in the presence of Zn octoate catalyst additive after 4h is significantly improved in terms of liquid distillate product fraction (between 75 – 75.5%), dark liquid residue (between 10.1 – 10.5%) and gaseous product (around 14.1 – 14.9%) (Runs 10 – 14). At 430°C, on increasing the run time to 4h, increase in the liquid distillate and dark liquid residue accompanied with a lowering of gas content is observed. In presence of increasing dosages of Zn octoate (from 32 to 64ppm active Zn content), the clear liquid distillate fraction increases to a maximum of 75.4% and dark liquid residue fraction increases to a maximum of 10.5%, in presence higher Zn octoate catalyst additive dosage (64ppm active Zn content). This indicates that higher dosages of Zn octoate catalyst additive promote the decomposition of the plastic component into the liquid distillate as well as the dark liquid residue at 430°C and prolonged run time. It should also be noted that as compared to blank runs, there is a significant improvement in the clear liquid distillate content from around 73% (for blank; Run 5) to around 75% (over Zn octoate catalyst additive; 32 and 64ppm active Zn content; Runs 8 and 9) and a lowering of the dark distillate content from around 12% (for blank; Run 5) to around 10% (over Zn octoate catalyst additive; 32 and 64ppm active Zn content; Runs 8 and 9). Even in the presence of catalyst additive, the gas fraction is around 14% is observed.

Hence we can conclude that at 430°C and 4h run time, in order to upgrade the liquid distillate fraction and simultaneously lower the dark liquid residue, higher dosage of Zn octoate catalyst additive (64ppm active Zn) is the catalyst of choice.

Reactions over Ca, Na and Fe naphthenate catalyst additives at 430°C:

Among naphthenate catalyst additives, Ca, Na and Fe naphthenate catalyst additives (at varying active Ca, Na and Fe content) have been evaluated at 430°C for varying dosage and reaction time (please see below Table 3.

TABLE III. MIXED LD PYROLYSIS PRODUCT DISTRIBUTION (%) AT AROUND 430°C, OVER METAL OCTOATE AND NAPHTHENATE CATALYST ADDITIVES AT VARYING ACTIVE CONTENT AND AT DIFFERENT REACTION TIME

No	PE (g)	Catal.	Catal. (ppm)	T (h)	Prod. Distr. (%)			
					A	B	C	D
5	60	Nil	NA	4	73	12.3	0	14.7
20	60	Na naph	32	4	75.3	10.6	0	14.1
21	60	Ca naph	32	4	74.4	10.7	0	14.9
6	60	Nil	NA	2	70.2	15.9	0	13.9
22	60	Ca naph	64	2	72.7	13.6	0	13.8
23	60		94	2	72.9	13.2	0	13.9
24	60		125	2	72.5	13.9	0	13.6
25	60		155	2	72.3	14.4	0	13.4
7	60	Nil	NA	1	62.3	23.1	0	14.6
26	60	Ca naph	64	1	63.2	23.9	0	12.9
27	60		94	1	63.3	23.4	0	13.4
28	60		125	1	61.4	25.6	0	13.1
29	60		155	1	62.9	24.4	0	12.7
30	60	Fe naph	64	2	70.2	16.1	0	13.7
31	60		94	2	70.8	14.9	0	14.3
32	60	Fe naph	64	1	62	25.3	0	12.7
33	60		94	1	62.6	26.1	0	11.3

A = clear liquid distillate; B = dark liquid residue; C= Coke; D= Gas

Reactions in presence of Ca naphthenate at 430°C:

From the data presented in Table 2, when Ca naphthenate is used as the catalyst additive, there occurs formation of clear liquid distillate, dark liquid residue and gas fractions as reaction products. Coke is not observed from 1 to 4h run time. Blank run (Run 7) conducted for 1h, shows a product distribution comprising 62.3% liquid distillate, 23.1% dark liquid residue and 14.6% gas. Product distribution profile for runs in the presence of Ca naphthenate catalyst additive after 1h is characterised by a liquid distillate product fraction (between 61 – around 63%), dark liquid residue (between 23 – around 25%) and gaseous product (between 12 – 13%) (Runs 26 – 29). At 430°C, in presence of increasing dosages of Ca naphthenate at 1h run time, a gradual lowering of formation of clear liquid distillate and gas component with a simultaneous increase in the dark liquid residue and decrease in the gas component is observed. In 1h run time at 430°C, highest liquid distillate formation is observed for Ca naphthenate (94ppm active Ca content).

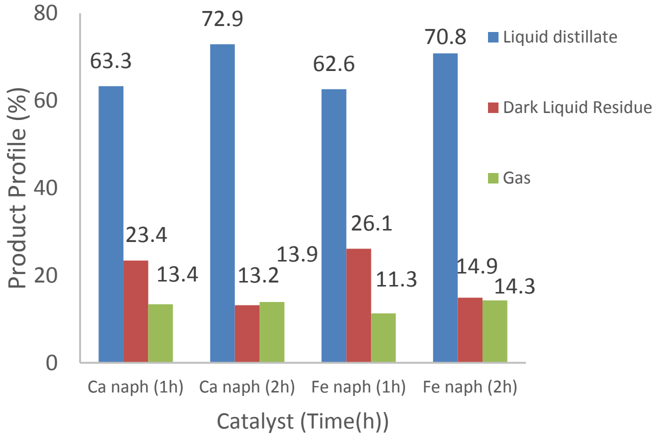

Figure 3. Catalyst relation to product profile

As the run time is increased from 1h to 2h, there is a considerable comparative change in the product distribution profile (compare runs 26 – 29 at 1h run time with Runs 22 – 25 at 2h run time). From the data presented in Table 2, in the presence of Ca naphthenate catalyst additive and at 430°C, 2h run time, here also there is formation of clear liquid distillate, dark liquid residue and gas fractions as reaction products. Coke is not observed at 2h run time. Blank run (Run 6) conducted for 2h shows a product distribution comprising 70.2% liquid distillate, 15.9% dark liquid residue and 13.9% gas. Product distribution profile for runs in the presence of Ca naphthenate catalyst additive after 2h are characterised by a liquid distillate product fraction (between 74 – 75%), dark liquid residue (between 13.2 – 13.9%) and gaseous product (around 13.4 – 13.9%) (Runs 22 – 25). At 430°C, on increasing the run time from 1h to 2h, increase in the liquid distillate accompanied with a gradual lowering of dark liquid residue content is observed, whereas the gas content at 2h run time is closely identical to that at 1h run time. In presence of increasing dosages of Ca naphthenate (from 64 to 155ppm active Ca content), the clear liquid distillate fraction increases to a maximum of 72.9% and gas fraction increases to a maximum of 13.9%, in presence of higher Ca naphthenate catalyst additive dosage (94ppm active Ca content). At 430°C and 2h run time, as the catalyst additive dosage progressively increases from 64ppm active to 155ppm active, the liquid formation is initially enhanced but decreases at extremely high dosages with increase in dark liquid residue.

On increasing the run time further to 4h, even on lowering the Ca naphthenate catalyst additive dosage, the product distribution profile comprises of clear liquid distillate, dark liquid residue and gas fractions. Coke is not observed at 4h run time. Blank run (Run 5) conducted for 4h, shows a product distribution comprising 73% liquid distillate, 12.3% dark liquid residue and 14.7% gas. Product distribution profile for runs in the presence of Ca naphthenate catalyst additive after 4h are characterised by a liquid distillate product fraction (between 74.4%), dark liquid residue (between 10.7%) and gaseous product (around 14.9%) (Runs 21). We can conclude that at 430°C and 2h run time, in order to upgrade the liquid distillate fraction and simultaneously lower the dark liquid residue, higher dosage (94ppm active Ca) of Ca naphthenate catalyst additive is the optimum.

Reactions in presence of Na naphthenate at 430°C:

From the data presented in Table 2, when Na naphthenate is used as the catalyst additive, there occurs formation of clear liquid distillate, dark liquid residue and gas fractions as reaction products. Blank run (Run 5) conducted for 4h, shows a product distribution comprising 73% liquid distillate, 12.3% dark liquid residue and 14.7% gas. Coke is not observed at 4h run time. At 4h run time, in presence of Na naphthenate catalyst additive (32ppm active Na content), the product distribution profile comprises liquid distillate product fraction (between 75.3%), dark liquid residue (between 10.6%) and gaseous product (around 14.1%) (Runs 20).

We can conclude that at 430°C and 4h run time, in order to upgrade the liquid distillate fraction and simultaneously lower the dark liquid residue, the optimum dosage of Na naphthenate catalyst additive is 32ppm active Na.

Reactions in presence of Fe naphthenate at 430°C:

From the data presented in Table 2, when Fe naphthenate is used as the catalyst additive, there occurs formation of clear liquid distillate, dark liquid residue and gas fractions as reaction products. Coke is not observed from 1 - 2h run time. Blank run (Run 7) conducted for 1h, shows a product distribution comprising around 62.3% liquid distillate, 23.1% dark liquid residue and 14.6% gas. Product distribution profile for runs in the presence of Fe naphthenate catalyst additive after 1h are characterised by a liquid distillate product fraction (62%), dark liquid residue (between 25 – around 26%) and gaseous product (between 11 – around 12%) (Runs 32 - 33). At 430°C, in presence of increasing dosages of Fe naphthenate at 1h run time, increase in formation of clear liquid distillate with a simultaneous decrease in the dark liquid residue and gas component is observed. At 430°C in 1h run time, highest liquid distillate formation is observed for Fe naphthenate (94ppm active Fe content).

As the run time is increase from 1h to 2h, there is a considerable comparative change in the product distribution profile (compare runs 32 - 33 at 1h run time with Runs 30 – 31 at 2h run time). From the data presented in Table 2, in the presence of Fe naphthenate catalyst additive at 430°C and 2h run time, here also there is formation of clear liquid distillate, dark liquid residue and gas fractions as reaction products. Coke is not observed at 2h run time. Blank run (Run 6) conducted for 2h shows a product distribution comprising 70.2% liquid distillate, 15.9% dark liquid residue and 13.9% gas. Product distribution profile for runs in the presence of Fe naphthenate catalyst additive after 2h are characterised by a liquid distillate product fraction (between 70.2 – 70.8%), dark liquid residue (between 14.9 – 16.1%) and gaseous product (around 13.7 – 14.3%) (Runs 22 – 25). At 430°C, on increasing the run time from 1h to 2h, increase in the liquid distillate accompanied with a gradual lowering of dark liquid residue content is observed, whereas the gas content at 2h run time increases. In presence of increasing dosages of Fe naphthenate (from 64 to 94ppm active Fe content), the clear liquid distillate fraction increases to a maximum of 70.8% and gas fraction increases to a maximum of 14.3%, in presence higher Fe naphthenate catalyst additive dosage (94ppm active Fe content). On the other hand highest formation of dark liquid residue is observed at lower dosages of Fe naphthenate catalyst additive (64ppm active Fe content) and extended run time. This indicates that higher dosages of Fe naphthenate catalyst additive promote the formation of the liquid distillate and gas fractions.

We can conclude that at 430°C and 2h run time, in order to upgrade the liquid distillate fraction and simultaneously lower the dark liquid residue, high dosage of Fe naphthenate catalyst additive (94ppm active Fe) is needed.

Mixed LD pyrolysis product distribution (%) over other metal catalysts additives at 430°C:

Data for product distribution (%) for the mixed LD pyrolysis in the autoclave at reaction temperature of 430°C are presented in Table 4, below.

Data presented in Table 4, relates to different metal catalyst additives that have been evaluated at 430°C, 4h run time in waste mixed LD pyrolysis. These are Zn oxide, Zn sulphide, γ-Alumina supported Ru- and Cu-oxides' catalysts. All these catalysts have been employed at dosage 32ppm active metal content. There occurs formation of clear liquid distillate, dark liquid residue and gas fractions as reaction products.

TABLE IV. MIXED LD PYROLYSIS PRODUCT DISTRIBUTION (%) AT 430°C, OVER OTHER METAL (ZN, RU, CU) CATALYST ADDITIVES AT 4H RUN TIME

No	PE (g)	Catal.	Catal. (ppm)	T (h)	Prod. Distr. (%)			
					A	B	C	D
5	60	Nil	NA	4	73	12.3	0	14.7
34	60	Zn oxide	32	4	75.2	10.5	0	14.3
35	60	Zn sulfide	32	4	73.5	13.8	0	12.7
36		Ru-Al2O3	32	4	75.9	11.1	0	13.1
37	60	Cu-Al2O3	32	4	74.4	10.7	0	14.9

A = clear liquid distillate; B = dark liquid residue; C= Coke; D= Gas

Coke is not observed in 4h run time. Blank run (Run 5) conducted for 4h, shows a product distribution comprising around 73% liquid distillate, 12.3% dark liquid residue and 14.7% gas. Product distribution profile for run in the presence of Zn oxide catalyst additive after 1h is characterised by a liquid distillate product fraction (75.2%), dark liquid residue (between 10.5%) and gaseous product (14.3%) (Run 34). Product distribution profile for run in the presence of Zn sulfide catalyst additive after 4h are characterised by a liquid distillate product fraction (73.5%), dark liquid residue (between 13.8%) and gaseous product (12.7%) (Run 35). Product distribution profile for runs in the presence of supported Ru-Alumina catalyst additive after 4h is characterised by a liquid distillate product fraction (75.9%), dark liquid residue (between 11.1%) and gaseous product (13.1%) (Run 36). Product distribution profile for runs in the presence of supported Cu-Alumina catalyst additive after 4h is characterised by a liquid distillate product fraction (74.4%), dark liquid residue (between 10.7%) and gaseous product (14.9%) (Run 37).

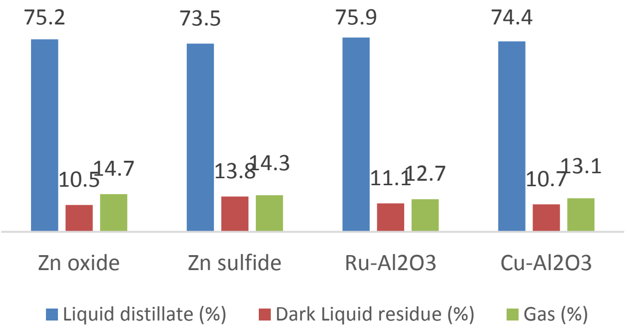

Figure 4. Product profile (%) for various metal catalysts

Hence we can conclude that at 430°C and 4h run time, in order to upgrade the liquid distillate fraction and simultaneously lower the dark liquid residue, Zn oxide (32ppm active Zn) or γ-alumina supported Ru oxide catalyst additive (32ppm active Ru) are the catalysts of choice.

Mixed LD pyrolysis product distribution (%) over metal octoate and naphthenate catalysts additives at 400°C:

Data for product distribution (%) for the mixed LD pyrolysis in the autoclave at reaction temperature of 400°C, are presented in Table 5, below.

TABLE V. MIXED LD PYROLYSIS PRODUCT DISTRIBUTION (%) AT 400°C, OVER METAL OCTOATE AND NAPHTHENATE CATALYST ADDITIVES AT 4H RUN TIME

No	PE (g)	Catal.	Catal. (ppm)	T (h)	Prod. Distr. (%)			
					A	B	C	D
38	60	Nil	NA	4	59.6	24.6	1.4	14.4
39	60	Zn octoate	9.8	4	61.2	23.5	0	15.3
40	60		19.6	4	64.2	22.6	0	13.2
41	60		30	4	65.3	22.4	0	12.3
42	60	Ce octoate	9.8	4	63.1	23.9	0	13.0
43	60	Ca naph	9.8	4	60.1	25.6	0	14.3
44	60	Fe naph	9.8	4	59.8	25.7	0	14.6

A = clear liquid distillate; B = dark liquid residue; C= Coke; D= Gas

Reactions over Zn octoate catalyst additives at 400°C:

From data presented in Table 5, at 400°C, runs have been conducted for 4h run time. Among octoate catalyst additives, Ce octaote and Zn octoate (varying active Zn content) catalyst additives have been evaluated at these reaction conditions. From the data presented in Table 5, when Zn octoate is used as the catalyst additive, there is formation of clear liquid distillate, dark liquid residue and gas fractions as reaction products. Coke is not observed at 4h run time for runs in presence of Ce or Zn octoates. Blank run (Run 38) conducted at 4h shows a product distribution comprising 59.6% liquid distillate, 24.6% dark liquid residue, 1.4% coke and 14.4% gas. Product distribution profile for runs in the presence of Zn octoate catalyst additive after 4h are characterised by a liquid distillate product fraction (between 61 – around 65%), dark liquid residue (between 22 – around 23%) and gaseous product (between 12 – 15%) (Runs 39 – 41). At 400°C, in presence of increasing dosages of Zn octoate at 4h run time, a gradual increase in formation of clear liquid distillate with a simultaneous decrease in the dark liquid residue and gas component is observed. In 4h run time at 400°C, highest liquid distillate formation is observed for Zn octoate (30ppm active Zn content).

From the data presented in Table 5, when Ce octoate is used as the catalyst additive, there is formation of clear liquid distillate, dark liquid residue and gas fractions as reaction products. Coke is not observed at 4h run time. Runs in the presence of Ce octoate catalyst additive after 4h are characterised by a liquid distillate product fraction (63.1%), dark liquid residue (2.93%) and gaseous product (13%) (Runs 42).

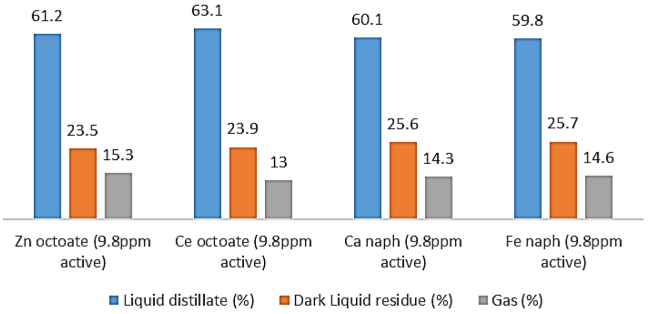

Figure 5. Product profile (%) at 400°C for metal octoate and napht catalysts (9.8 ppm active metal content)

Hence we can conclude that at 400°C and 4h run time, in order to upgrade the liquid distillate fraction and simultaneously lower the dark liquid residue, higher dosage of Zn octoate catalyst additive 30ppm active Zn is optimum dosage.

Reactions over Ca and Fe naphthenates at 400°C:

From data presented in Table 5, at 400°C, runs have been conducted for 4h run time. Among naphthenate catalyst additives, Ca and Fe naphthenates (active Ca and /or Fe content = 9.8ppm) catalyst additives have been evaluated at these reaction conditions. From the data presented in Table 5, when Ca naphthenate is used as the catalyst additive, there is formation of clear liquid distillate, dark liquid residue and gas fractions as reaction products. Coke is not observed at 4h run time for runs in presence of Ca or Fe naphthenates. Blank run (Run 38) conducted at 4h shows a product distribution comprising 59.6% liquid distillate, 24.6% dark liquid residue, 1.4% coke and 14.4% gas. Product distribution profile for runs in the presence of Ca naphthenate catalyst additive (9.8ppm active) after 4h are characterised by a liquid distillate product fraction (between 60.1%), dark liquid residue (between 25.6%) and gaseous product (between 14.3%) (Runs 43). Product distribution profile for runs in the presence of Fe naphthenate catalyst additive (9.8ppm active) after 4h are characterised by a liquid distillate product fraction (59.8%), dark liquid residue (between 25.7%) and gaseous product (between 14.6%) (Runs 44).

Hence we can conclude that at 400°C and 4h run time, in order to upgrade the liquid distillate fraction and simultaneously lower the dark liquid residue, Ca naphthenate catalyst additive (9.8ppm active Ca) is the catalyst of choice.

Mixed LD pyrolysis product distribution (%) over metal octoate and naphthenate catalysts additives at 360°C:

Data for product distribution (%) for the mixed LD pyrolysis in autoclave at reaction temperature of 360°C are presented in Table 6.

TABLE VI. DATA FOR PRODUCT DISTRIBUTION (%) FOR THE MIXED LD PYROLYSIS IN AUTOCLAVE AT REACTION TEMPERATURE OF 360°C

No	PE (g)	Catal.	Catal. (ppm)	T (h)	Prod. Distr. (%)			
					A	B	C	D
45	60	Nil	NA	4	21.9	69	0.8	8.3
46	60	Zn octoate	9.8	4	28.5	60.4	0	11.1
47	60		19.6	4	29.1	59.4	0	11.5
48	60	Ce octoate	9.8	4	25.5	63.9	0	10.6
49	60	Cu octoate	9.8	4	25.7	60.9	0	13.4
50	60	Ca naph	9.8	4	21.1	68.8	0.7	9.4
51	60	Na naph	9.8	4	25.9	65	0	9
52	60	Fe naph	9.8	4	25.8	64.0	0	10.2
53	60	Mg naph	9.8	4	26.8	62.9	0	10.3

A = clear liquid distillate; B = dark liquid residue; C= Coke; D= Gas

Reactions over Zn octoate catalyst additives at 360°C:

From data presented in Table 6, at 360°C, runs have been conducted for 4h run time. Among octoate catalyst additives, Ce, Cu and Zn octoate (varying active Zn content) catalyst additives have been evaluated at these reaction conditions. From the data presented in Table 6, when Zn octoate is used as the catalyst additive, there is formation of clear liquid distillate, dark liquid residue and gas fractions as reaction products. Coke is not observed for 4h run time. Blank run (Run 45) conducted for 4h, shows a product distribution comprising 21.9% liquid distillate, 69% dark liquid residue, 0.8% coke and 8.3% gas. Product distribution profile for runs in the presence of Zn octoate catalyst additive (9.8 and 19.6ppm active) after 4h are characterised by a liquid distillate product fraction (between 28 – around 29%), dark liquid residue (between 59 – around 60%) and gaseous product (around 11 %) (Runs 46 – 47). At 360°C, in presence of increasing dosages of Zn octoate and 4h run time, a gradual increase in formation of clear liquid distillate with a simultaneous decrease in the dark liquid residue and increase in the gas component is observed. In 4h run time at 360°C, highest liquid distillate formation is observed for Zn octoate (19.6ppm active Zn content).

Product distribution profile for runs in the presence of Ce octoate catalyst additive (9.8ppm active) after 4h are characterised by a liquid distillate product fraction (between 25.7%), dark liquid residue (between 60.9%) and gaseous product (around 13.4%) (Runs 49). Product distribution profile for runs in the presence of Cu octoate catalyst additive (9.8ppm active) after 4h are characterised by a liquid distillate product fraction (between 28 – around 29%), dark liquid residue (between 59 – around 60%) and gaseous product (around 11 %) (Runs 46 – 47). Hence we can conclude that at 360°C and 4h run time, in order to upgrade the liquid distillate fraction and simultaneously lower the dark liquid residue, Zn octoate catalyst additive (19.6ppm active Ca) is the catalyst of choice.

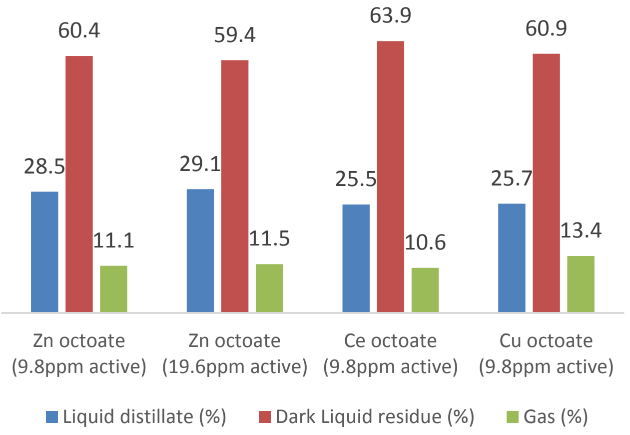

Figure 6. Product Profile (%) at 360°C for metal octoate catalysts

Reactions over Ca, Na, Fe and Mg naphthenate catalyst additives at 360°C:

Runs have been conducted at 360°C for 4h run time and data presented in Table 6. Among naphthenate catalyst additives, Ca. Na, Fe and Mg naphthenate catalyst additives (9.8ppm active metal content) have been evaluated at these reaction conditions. From the data presented in Table 6, when these naphthenate catalyst additives are used, there is formation of clear liquid distillate, dark liquid residue and gas fractions as reaction products. Coke is only observed for Ca naphthenate but not for the other naphthenates at 4h run time. Blank run (Run 45) conducted for 4h, shows a product distribution comprising 21.9% liquid distillate, 69% dark liquid residue, 0.8% coke and 8.3% gas. Product distribution profile for runs in the presence of Ca naphthenate catalyst additive after 4h is characterised by a liquid distillate product fraction (21.1%), dark liquid residue (68.8%), coke (0.7%) and gaseous product (9.4 %) (Run 50).

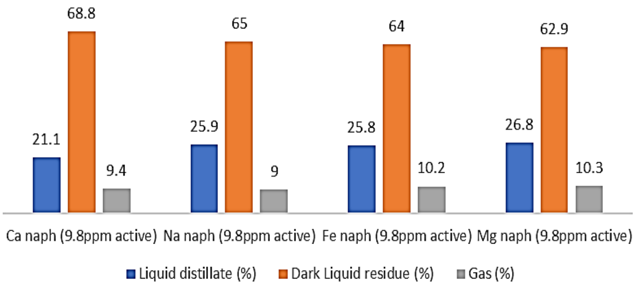

Figure 7. Product Profile (%) at 360°C for metal naphthenate catalysts

Product distribution profile for runs in the presence of Na naphthenate catalyst additive after 4h is characterised by a liquid distillate product fraction (25.9%), dark liquid residue (65%), and gaseous product (9%) (Run 51). Product distribution profile for runs in the presence of Fe naphthenate catalyst additive after 4h is characterised by a liquid distillate product fraction (25.8%), dark liquid residue (64%), coke (0.7%) and gaseous product (10.2%) (Run 52). Product distribution profile for runs in the presence of Mg naphthenate catalyst additive after 4h is characterised by a liquid distillate product fraction (26.8%), dark liquid residue (62.9%) and gaseous product (10.3%) (Run 53).

Hence we can conclude that at 360°C and 4h run time, in order to upgrade the liquid distillate fraction and simultaneously lower the dark liquid residue, Fe naphthenate and Mg octoate catalyst additive (9.8ppm active Mg) are optimum choice.

IV. SUMMARY

Our principle objective is to provide an economic and sustainable solution for conversion of waste plastic to useful hydrocarbon products via catalytic pyrolysis. The catalytic pyrolysis route reported by us in this report is environmentally friendly as it has the potential to lower the carbon-footprint for plastics, with the consumption of undesired plastic waste and generating of heavy metal contaminant free, hydrocarbon fuel alternatives.

Summarizing the investigations, catalytic pyrolysis of waste mixed low density plastic has been performed in an autoclave fitted with distillation apparatus, at 360, 400, 430 and >455°C and varying dosages of some metal catalyst additives at varying reaction time. In this report, metal catalyst additives evaluated in waste mixed low density plastic conversion are some metal octoates, metal naphthenates, metal oxides, metal sulfides and γ-alumina supported metal oxide catalysts. These metal catalyst additives, at respective inherent specific dosages, play a fundamental role in influencing the product distribution profile of the catalytic pyrolysis of waste low density mixed plastic. The catalyst additives selectively promote the formation of certain product components via chemical decomposition (cracking) of the plastic substrate while simultaneously inhibiting the formation of other reaction products. Comparative evaluation of product distribution profiles in the presence and absence of catalyst additives indicates the advantage of using catalyst additives. From our experimental data, another influencing parameter of paramount importance, on the nature of reaction products formed during reaction, is the reaction temperature. At reaction temperature = between 360 – 430°C, formation of a dark liquid residue is observed, and for most catalyst additives, coke formation is completely suppressed. At lower (1h) run time in the presence of catalyst additives, at inherently specific dosages, consecutive cracking of hydrocarbon chains is initiated. This may result in a step-wise process at the molecular level with larger hydrocarbon chains being the first to be cracked into smaller chain-length distillate molecules, which would be progressively cracked as a function of time. This may account for formation of larger liquid distillate and gas contents at our reaction conditions, at extended run time. On removal of liquid and gas components from the autoclave at the completion of conversion process, there remains behind within the autoclave a significant amount of dark liquid distillate, a polymer-like entity of difficult-to-crack hydrocarbons, with molecular weights between around 230 – 1100 amu (>20%) as observed at lower run time (1h). However as run times are further increased to 2h and 4h, more clear liquid distillate and gas content (%) are observed and at 4h run time dark liquid formation is observed to be significantly suppressed (around 10-12%), at our reaction conditions. It may be noted that formation of dark residue can be suppressed using a suitable catalyst additive- (higher) dosage combination. An exception of Ca naphthenate catalyst additive (low dosage) in whose presence coke is formed even at comparatively low reaction temperature of 360°C stresses on the importance of choice of temperature-catalyst additive (and dosage). At higher reaction temperature (>455°C), dark liquid residue formation is completely suppressed and high selectivity for the liquid distillate fraction is observed. It is observed that higher temperature and greater run times may allow for the build-up of coke and gaseous components; at our reaction conditions, formation of coke may be initiated at reaction temperature >455°C. Investigations at increasing run times indicate that at our reaction conditions, the catalytic pyrolysis of waste low density plastic appears to be principally influenced by a combination of type of catalyst additives, their dosage and the reaction temperature.

V. CONCLUSION

In conclusion a catalyst mediated pyrolysis route to eliminating waste plastic by converting it to useful hydrocarbon fuel alternatives has been detailed. Principal influencers of the waste plastic pyrolysis at our reaction conditions are nature of catalyst additive, its dosage and temperature with run time being a secondary influencer. The catalyst additives direct the improvement of desired liquid and gaseous fractions. A suitable ‘temperature - catalyst additive-catalyst dosage’ combination can significantly suppress the formation of undesired dark liquid residue and coke fractions.

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