ORIGINAL PAPER

Estimation of pyrolysis product of LDPE degradation using different process parameters in a stirred reactor

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ABSTRACT

Pyrolysis of low density polyethylene (LDPE) by equilibrium fluid catalytic cracking (FCC) was studied in a stirred reactor under different process parameters. In this work, the effect of process parameters such as degradation temperature (420-510°C), catalyst/polymer ratio (0-60%), carrier gas type (H_2, N_2, ethylene, propylene, Ar and He), residence time and agitator speed (0-300 rpm) on the condensate yield (liquid, gas and coke) and product composition were considered. Reaction products were determined by GC analysis and shown to contain naphthenes (cycloalkanes), paraffins (alkanes), olefins (alkenes) and aromatics. Higher temperature and more catalyst amount enhanced LDPE cracking. The maximum "fuel like" condensed product yield was attained at 450°C and 10% catalyst, respectively and gaseous products increased with increases in temperature. Hydrogen as a reactive carrier gas increased the condensed and paraffinic product yield. Appropriate heat transfer (by stirring) increased the catalyst efficiency in a stirred reactor. **Polyolefins J (2015) 2: 39-47**

Keywords: LDPE; pyrolysis; fluid catalytic cracking (FCC); stirred reactor; carrier gas; agitator speed

INTRODUCTION

Owing to their versatility and low cost, consumption of plastic products has seen an extensive increase over the past few decades. With a yearly consumption of nearly 100 kg of plastics per person, the management of this vast waste stream represents a matter of great social and environmental concern [1]. Feedstock recycling currently represents an area of increasing scientific interest with prospects to absorb a large amount of waste plastics [2, 3].

Thermal degradation of polymers has great interest as an alternative source of energy or chemical raw materials, as well as its contribution to the solution of environmental problems [4]. Thermal cracking involves the scission of long polymer molecules simply by exposure to high temperatures under inert atmospheric conditions. This type of process generates a heterogeneous hydrocarbon (HC) mixture, whose precise composition depends primarily on process

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conditions and plastic type [5–8]. This term covers a number of processes (pyrolysis, gasification, catalytic cracking, de-polymerization, and dehydrogenation) designed to convert plastic wastes into petrochemical feedstock for use in the production of refined chemicals or fuels [3].

Pyrolysis is generally defined as the controlled burning or heating of a material in the absence of oxygen [9] whereas catalytic pyrolysis can improve the product selectivity and reduce the energy input [7]. Most previous studies on the catalytic pyrolysis of waste plastics have used micro-porous materials [10]. The catalytic degradation of polymeric materials has been reported for a range of catalysts centered on the active components in a range of different model catalysts, such as amorphous silica–aluminas, zeolites Y, ZSM-5 and various acidic catalysts and particularly the new family of MCM materials [11–24]. However, these catalysts; even if performing well are considered unfeasible from the point of view of practical use due to the manufacturing cost and the high receptiveness of the process to the cost of the catalyst.

An economical improvement of processing the recycling via catalytic cracking would be to operate in mixing the polymer waste with utilized fluid catalytic cracking (FCC) of commercial catalysts. These catalysts increase significantly the commercial potential of a recycling process based on catalytic degradation, as cracking catalysts could cope with the conversion of plastic waste co-fed into a refinery FCC unit [9, 25–26].

Temperature is likely the most important variable affecting the catalytic cracking of plastics [14]. The literature shows the strong dependence of the carbonization products to the main process parameters such as final temperature, catalyst type and polymer/catalyst ratio, pressure, heating rate and residence time [15]. However, other process parameters like carrier gas and agitator speed as affecting mass and heat transfer respectively, are limited [14-15].

Liquefaction of waste plastics in high temperature and pressure reactors in the presence of H_2 or a hydrogen donor (such as tetralin or oil) in the presence of catalysts has been studied [27]. Stirring of the melt in a pyrolysis vessel greatly accelerates the heat transfer process and it can help the process towards better energy saving. Discontinuous (batch process) and continuous (alternating batch or cascade) stirred reactors are generally used in commercial-scale melt-phase pyrolysis plants. These units are relatively simple, consisting of a large stainless steel vessel with indirect heating (either flame or hot air), a large stirrer and possibly internals such as baffles to enhance mixing and heat exchanger surfaces [28].

The aims of this study are to investigate the effect of (i) degradation temperature, (ii) FCC catalyst concentration, (iii) reactor stirrer speed and (iv) carrier gas type in relation to the product yield and composition in catalytic pyrolysis of LDPE. GC analysis has been used to determine product composition.

EXPERIMENTAL

Material

LDPE (Bandar Imam Petrochemical Company, Mahshahr, Iran), ethylene and propylene (purity 99.9%, Tehran Petrochemical Company, Tehran, Iran), N_2, Ar, H_2 and He (purity 99.99%, Roham Co) were used as received. The FCC catalyst (Table 1) was regenerated prior to use.

Analyzer instruments

GC analyses were performed on a Varian CP-3800 GC fitted with a flame ionization detector (at 280°C) and Varian CP-8200 autosampler. Separation was achieved using a VF-5 MS capillary column (30 m ~ 0.25 mm I.D, Varian) with a temperature program of 200°C (4 min) then heated to 280°C (7 min) at a rate of 10°C min-1 and He as the carrier gas (1.0 mL/min^{-1}). The identity of compounds was confirmed with known standards, special software and highly efficient GC.

pyrolysis process

Pyrolysis experiments were carried out in a 1 L stirred semi-batch reactor (Buchi pilot plant with a custom built reactor) under atmospheric pressure and the

Table 1. The specification of utilized FCC catalyst in catalytic degradation of low density polyethylene

Surface area (BET)	235 m^2/g
SiO_2	80.10%
Al_2O_3	13.40%
Na	0.30%
Ca	1.54%
Si/Al	6
Fe	0.20%
V (ppm)	450
Ni (ppm)	180

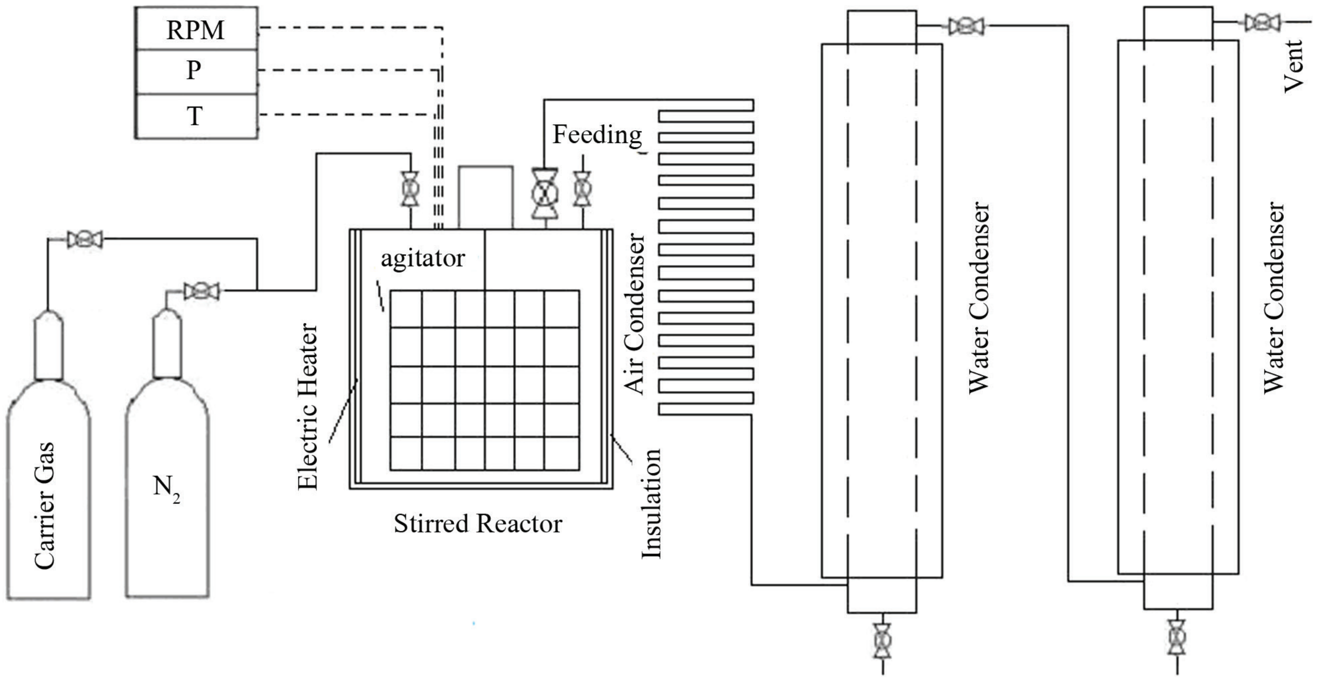

Figure 1. Flow scheme of the laboratory stirred reactor

schematic diagram is shown in Figure 1. The fixed experimental conditions are as follows: LDPE (100 g), FCC catalyst and carrier gas stream (300 mL/min), heating rate (25°C/min) up to the final temperature. The non-condensable products were vented after cooling through three condensers. The condensed HCs products were stored in glass sampling bottles. The components of total condensed HCs (residue in the condensers contained C3 to C15) were quantified by gas chromatography (GC). The non-condensable products were not analyzed. The solid char yield was determined gravimetrically after completion of the reaction. The non-condensable yield was calculated by subtracting the weight of the condensed HC and solid products from the sample weight.

RESULTS AND DISCUSSION

Mass balance of LDPE pyrolysis products (condensable products, solid residue and non-condensable by difference) was determined gravimetrically (Tables 2-9) for the reactor variables of temperature (420-510°C), FCC catalyst/PP ratio (0-60%), stirrer rate (0-300 RPM) and carrier gas (N_2, H_2, He, Ar, ethylene and propylene).

Effect of the degradation temperature

The effect of degradation temperature on the catalytic pyrolysis of LDPE was examined at 420, 450, 480 and 510°C. Table 2 shows the product yields (condensed, non-condensable and coke) obtained in the LDPE pyrolysis experiments. The main product fraction obtained was condensed hydrocarbons with yields up to 91.5%. As the pyrolysis temperature increased the coke yield also increased. At 510°C, the coke and non-condensable show a maximum yield, although the condensed hydrocarbons show a maximum peak at 450°C. Jung et al. [18] have observed a decrease in pyrolytic liquid with temperature, while other studies have witnessed a peak in liquid yield with temperature [29-30].

The composition of the condensed products from the catalytic degradation of LDPE over spent FCC catalyst in a semi-batch stirred reactor, as a function of temperature, is given in Table 3. These components are grouped into different organic compound classes, i.e., naphthenes (cycloalkanes), paraffins (alkanes),

Table 2. The effect of temperature on the product yield

Temperature (°C)	Condensed fuel (%)	Non-condensable product (%)	Coke (%)
420	87.6	8.6	3.8
450	91.5	4.4	4.1
480	86.3	9.3	4.4
510	82.7	11.4	5.9

Ratio of catalyst/polymer: 20% (w/w), agitator speed: 50RPM, carrier gas: N_2

olefins (alkenes) and aromatics. The results show that aromatics (11.6-16.4%) and olefin to paraffin ratio (1.58-2.55) increase with increasing temperature. The average molar mass and distribution of C number of condensed hydrocarbons versus LDPE degradation temperature are given in Table 4. The results show that the C number distribution of the condensed products shifts to lighter hydrocarbons with temperature and the average molar mass decreases. Meanwhile, the gasoline range products reach their maximum yield at 510°C (83.2%), although Lin et al. [31] showed a decrease in gasoline range products with temperature in a gas phase reactor.

Quantitative analyses of the condensed HCs were obtained from 420°C, since LDPE was converted to condensed products, dominated by aliphatic HCs (olefins at 51.3% and paraffins at 32.5%). Aromatics (11.6%) and naphthenes (4.63%) constituted the lower shares in the products. In light fuels like gasoline, the C5 to C9 fractions are highly desirable feedstocks. This gasoline fraction constituted 76.5% of the condensed product. The gasoline yield was shown to increase with temperature. In addition, the C7 yield was 20.8% as the dominant C number in the condensed HCs.

At 450°C, the condensed product was composed of olefins (53.8%), paraffins (28.1%) and aromatics (14.7%). The condensed product had a C3 to C13 distribution with the main compounds being C7 at 22.9%. At 480°C, the quantity and composition of olefins (C3-C13) in the condensed fraction were enhanced by 55.3% of the condensed HCs of which 24.4% was C7. The data clearly shows that the reduction in naphthene and paraffin yields favors the formation of double bonds, an indication that, unsaturation, cyclization and aromatization occur around 480°C. While at 510°C, the condensed HCs decrease by about 9% and can reach 82.7% yield of which 24.3% was C7. The predominant process at higher temperature involves the conversion of liquid products directly to aromatics and some gases, and the stripping of gases to form aromatics and finally char. It appears that this conversion can be actively used at elevated temperatures in some reactions, such as in the Diels–Alder reaction. The formation of aromatics in the pyrolysis of polyolefin is accomplished using the Diels–Alder reaction, followed by dehydrogenation [18, 32-33]. The detailed mechanism of the formation of BTX aromatics is presented in some published papers [7, 18].

Table 3. The effect of temperature on the condensed product composition

Type in total	Temperature (°C)			
	420	450	480	510
Olefins	51.27	53.82	55.29	57.14
Paraffins	32.49	28.08	25.43	22.4
Naphthenes	4.63	3.36	3.87	4.11
Aromatics	11.61	14.74	15.41	16.35
Olefin/paraffin	1.58	1.92	2.17	2.55

Ratio of catalyst/polymer: 20% (w/w), agitator speed: 50RPM, carrier gas: N_2

Table 4. The effect of temperature on the carbon number distribution of the condensed product composition

	420	450	480	510
C3	0.943	0.975	1.032	1.231
C4	7.834	8.219	8.765	8.975
C5	14.654	16.632	17.342	17.686
C6	12.435	13.259	14.096	17.742
C7	20.768	22.845	24.387	24.272
C8	14.364	13.057	12.525	12.097
C9	14.243	13.232	12.234	11.365
C10	7.032	6.584	5.708	3.391
C11	4.261	3.069	2.354	1.954
C12	2.572	1.689	1.194	0.971
C13	0.843	0.4	0.334	0.295
C14	0.051	0.039	0.029	0.021
Sum (C5-C9)	76.464	79.025	80.584	83.162
Avg. molecular weight	102.66	99.48	97.38	94.88

Ratio of catalyst/polymer: 20 % (w/w), agitator speed: 50RPM, carrier gas: N_2

Effect of the spent FCC catalyst

The overall effect of increasing the catalyst/LDPE ratio from 1:10 to 6:10 on the product was small but predictable. As the ratio of catalyst to plastics increases, the possibility of contact time and area between the polymer and catalyst increases and the catalyst can perform better on the product distribution although the total product yield decreased slightly after a 6-fold increase in catalyst. Generally, the high surface area catalysts can change the nature of the pyrolysis and affect the composition and yields even at low levels [24, 34].

This can be attributed to the sufficient cracking ability of the catalyst, reasonable mixing (50 RPM) and excellent contact between the plastics and catalyst particles.

The results show a maximum condensed product yield when catalytic pyrolysis was performed in the presence of 10% utilized FCC catalyst. Table 5 shows

Table 5. The effect of catalyst/polymer ratio on the product yield

Catalyst/ Polymer (% w/w)	Condensed product (%)	Non-condensable product (%)	Coke (%)
10	93.2	4.5	2.3
20	91.5	4.4	4.1
40	86.5	7.6	5.9
60	79.7	13.1	7.2

T: 450°C, agitator speed: 50 RPM, carrier gas: N_2

the yield versus catalyst load at 450°C under N_2.

The results show that catalyst has no obvious effect on the non-condensable products although it seems that addition of catalyst increases the gaseous and coke products. Coke formation may be attributable to the aromatization and dehydrogenation and increases coke on the catalyst surface.

The condensed HCs yields and composition at different spent FCC loadings are given in Table 6. HC analysis shows that the main components were olefins (52-56%), paraffins (31-24%), aromatics (<17%) and naphthenes (3.4-4.0%). These results indicate that dehydrogenation increases with catalyst loading and the aromatic products and olefin/paraffin ratio increase with it as well.

The average molar mass and carbon number distribution of the condensed HCs obtained from FCC pyrolysis of LDPE at similar conditions were compared at different catalyst ratios given in Table 7. The results show that the FCC catalyst decreases the molar mass of the condensed product. Furthermore, as the catalyst/polymer ratio increases the molecular size becomes selective and this is reflected in the gasoline section (C5- C9) which has a greater proportion (84.4%) in the final condensed HCs at the highest level of catalyst used. In other words, when more catalyst was added a higher gasoline yield was obtained (75-85%) because of the appropriate size selectivity by the pore size of the catalyst.

The degradation of high molar mass olefinics occurs over the catalyst surface forming smaller molecular fragments that can diffuse into the pores of the zeolites for further cracking and selectivity. Diffusion of these cracked molecules within the catalyst is greatly influenced by pore size constraints which similarly depends on the pore and channel configurations [35-37].

Table 6. The effect of catalyst/polymer ratio on the condensed product composition

Type (each in total)	Catalyst/polymer ratio (%)			
	10	20	40	60
Olefins	52.95	53.82	54.32	55.28
Paraffins	30.16	28.08	26.49	24.77
Naphthenes	3.97	3.36	3.46	3.84
Aromatics	12.92	14.74	15.73	16.11
Olefin/Paraffin	1.76	1.92	2.05	2.23

T: 450°C, agitator speed: 50 RPM, carrier gas: N_2

Table 7. The effect of catalyst/polymer ratio on the carbon number distribution of the condensed product composition

	10	20	40	60
C3	1.03	0.975	1.051	1.086
C4	8.681	8.219	8.767	9.234
C5	15.787	16.632	17.546	18.165
C6	14.623	13.259	13.683	14.087
C7	21.842	22.845	23.001	22.781
C8	13.465	13.057	14.923	15.244
C9	9.786	13.232	13.423	14.157
C10	9.354	6.584	4.231	3.265
C11	3.318	3.069	2.604	1.393
C12	1.554	1.689	0.406	0.358
C13	0.496	0.4	0.336	0.213
C14	0.064	0.039	0.029	0.017
Sum (C5-C9)	75.503	79.025	82.576	84.434
Avg. molecular weight	99.65	99.48	97.02	95.59

T: 450°C, agitator speed: 50 RPM, carrier gas: N_2

These results show that condensed HCs were distributed from C3 to C13 compounds although catalyst addition tended to show a condensed product with narrower carbon number distribution. C7 was the main component (21.8-23%) in the condensed product.

Effect of carrier gas

Table 8 shows the product yields (condensed, non-condensable and coke) obtained from FCC LDPE pyrolysis using different carrier gases. The addition of H_2 resulted in condensed HC yield increase from 49.5% (with no gas) to 96.1%. These results are in agreement with those obtained by William and Slaney

Table 8. The effect of carrier gas on the product yield

Carrier gas	Molecular weight	Condensed product (%)	Non-condensable product (%)	Coke (%)
H_2	2	96.1	3.6	0.3
He	4	93.1	4.8	2.1
N_2	28	91.5	4.4	4.1
Ethylene	28	93.8	4.5	1.7
Propylene	42	89.2	8.6	2.2
Argon	37	86.4	8.3	5.3
Without carrier Gas	∞	49.5	31.1	19.4

T: 450°C, agitator speed: 50 RPM, carrier gas: N_2

Table 9. The effect of carrier gas on the condensed product composition

Type (each in total)	Carrier gas					
	N_2	He	Ar	Ethylene	Propylene	H_2
Olefins	53.82	49.67	56.24	52.17	54.32	43.21
Paraffins	28.08	39.54	24.54	34.26	27.96	49.76
Naphthenes	3.36	3.21	3.48	3.79	4.44	2.65
Aromatics	14.74	7.58	15.74	9.78	13.28	4.38
Olefin/Paraffin	1.92	1.26	2.29	1.52	1.94	0.87

T: 450°C, agitator speed: 50 RPM, carrier gas: N_2

[27] and previous work on the LLDPE and HDPE pyrolysis [14-15].

Reactivity is specifically defined in this work as the ability of carrier gas to take part in the pyrolysis process. The process without carrier gas acts like the condition with an infinitive molar mass carrier gas which does not carry the products. The results show that the condensed product yield decreased in the absence of carrier gas.

Neutral carrier gas

The neutral carrier gas (N_2, He or Ar) does not take part in the process and just carries the vaporizable products of the reactor. The results show that the carrier gases with lower molar mass have more ability to carry the products since they have higher acceleration (Table 8). The higher acceleration helps to carry more of the evaporated products of the reactor. Furthermore, the neutral carriers help to protect the pyrolysis products of more dehydrogenation and cracking and therefore increase the condensed HCs and saturated components. The use of He (low molar mass) gave lower olefin/paraffin ratio, olefin and aromatic components in comparison with Ar and N_2.

Reactive carrier gas

H_2, ethylene and propylene are examples of reactive carrier gases, although H_2 has more reactivity. H_2 reacts, via hydrogenation, with the pyrolysis products to protect them from more chain scission and thus produces a proportion of liquid HCs (Table 8). The results show that the reactivity of the carrier gas can affect coke formation. Addition of a reactive carrier gas decreases coke formation by protection from aromatization and dehydrogenation. The use of H_2 decreased coke yield from 19.4% (without carrier gas) to 0.3 %.

Table 9 shows the variation of the condensed HC composition with respect to different carrier gases. The results show that the paraffins increased with addition of H_2 or ethylene and propylene, while the aromatics products decreased with these reactive carrier gases.

The carbon number distribution and average molar mass of condensed HC of LDPE degradation for each carrier gas is given in Table 10. It appears that the condensed HC shifted to lower molar mass in the

Table 10. The effect of carrier gas on the carbon number distribution of the condensed product composition

	N_2	He	Ar	Ethylene	Propylene	H_2
C3	0.975	0.934	1.02	1.13	1.01	1.243
C4	8.219	8.453	9.263	8.943	9.132	10.324
C5	16.632	16.814	15.793	15.724	14.264	16.835
C6	13.259	14.73	12.297	13.635	12.874	14.354
C7	22.845	21.124	22.764	24.147	23.564	24.265
C8	13.057	14.395	13.793	13.125	14.234	14.043
C9	13.232	14.125	12.983	12.784	14.276	12.137
C10	6.584	4.896	6.419	5.656	6.403	3.069
C11	3.069	2.785	3.183	3.131	2.544	2.391
C12	1.689	1.423	1.925	1.352	1.412	0.964
C13	0.4	0.287	0.511	0.327	0.239	0.352
C14	0.039	0.034	0.049	0.046	0.048	0.023
Sum(C5-C9)	79.025	81.188	77.63	79.415	79.212	81.634
Avg. molecular weight	99.48	98.43	99.7	98.55	99.57	95.69

T: 450°C, agitator speed: 50 RPM, carrier gas: N_2

gasoline range with decreasing carrier gas molar mass as well as an increase of the reactivity. Using a higher molar mass carrier gases gave a slightly broader carbon number distribution with C7 compounds being the main component (21.1-24.3%).

Mechanism

The use of a reactive carrier gas can take part in the process and these gases influence the equilibrium transition of gaseous towards liquid products [14-15]. H_2, ethylene and propylene can take part in the pyrolysis process at high temperatures.

Effect of agitator speed

Table 11 shows the yield of the pyrolysis of LDPE in relation to process agitator speed. At 50 RPM, agitator speed resulted in maximum condensed HC yields, especially at 450°C. In the reactors with the high viscosity polymer melts, a temperature gradient was observed from the wall (highest) to the reactor center (lowest).

Appropriate agitator design and speed can influence the temperature gradient and uniformity. The composition of the condensed HCs as a function of agitator speed is given in Table 12. It can be observed that the olefin/paraffin ratio and aromatic decreased with agitator speed. An increase in agitator speed can decrease the process time and polymer chains have lower residence time in the reactor. The shorter residence time minimizes polymer chain scission and dehydrogenation. Table 13 shows that agitator speed has had no obvious effect on the molar mass of condensed HC although gasoline range product yield was greatest at 50 RPM. The condensed HCs ranged between C3 and C13 compounds and C7 was the main component (21.4-23 %).

Table 11. The effect of agitator speed on the product yield

RPM	Condensed product (%)	Non-condensable product (%)	Coke (%)
0-without stirrer-	64.2	26	9.8
0	85.3	9.5	5.2
50	91.5	4.4	4.1
100	87.3	9.5	3.2
300	82.2	15.4	2.4

T: 450°C, Catalyst/ Polymer: 20% (W/W), Carrier gas: N_2

Table 12. The effect of agitator speed on the condensed product composition

Type (each in total)	Agitator speed (RPM)			
	0	50	100	300
Olefins	57.31	53.82	50.47	48.32
Paraffins	22.63	28.08	33.56	36.31
Naphthenes	4.64	3.36	3.79	3.92
Aromatics	15.42	14.74	12.18	11.45
Olefin/Paraffin	2.53	1.92	1.5	1.33

T: 450°C, Catalyst/ Polymer: 20% (W/W), Carrier gas: N_2

Table 13. The effect of agitator speed on the carbon number distribution of the condensed product composition

	0	50	100	300
C3	1.223	0.975	1.012	1.125
C4	9.295	8.219	8.786	9.423
C5	13.465	16.632	15.934	15.214
C6	12.693	13.259	13.604	12.892
C7	21.421	22.845	23.013	21.754
C8	12.462	13.057	14.313	13.032
C9	12.198	13.232	11.214	11.787
C10	7.497	6.584	6.735	7.126
C11	4.385	3.069	3.341	3.531
C12	4.239	1.689	1.467	3.546
C13	0.994	0.4	0.554	0.521
C14	0.128	0.039	0.027	0.049
sum(C5-C9)	72.239	79.025	78.078	74.679
Avg. Molecular Weight	102.98	99.48	99.15	100.83

T: 450°C, Catalyst/ Polymer: 20% (W/W), Carrier gas: N_2

The reactor without stirrer

Table 11 shows the product yields of LDPE pyrolysis with and without reactor stirring. The results show that agitation can improve the heat transfer within the reactor. With no agitation, the weak radiation heat transfer causes plastic agglomeration in the center of the reactor to occur. Poor heat transfer decreases the efficiency of the catalyst and increases the undesirable products such as char and gaseous products [14-15, 18, 38].

CONCLUSION

A laboratory catalytic stirred system has been used to obtain a range of volatile hydrocarbons by catalytic degradation of LDPE in the temperature range 420-510°C. The stirred reactor system has a number of advantages in the pyrolysis of LDPE by improved mass and heat transfer. The selection of carrier gas was shown to greatly influence HC yields and composition. Neutral carrier gases gave high condensate yields, while reactive gases can influence paraffin yields. The catalytic degradation of LDPE over the spent commercial FCC equilibrium catalyst was shown to be effective for the production of potentially valuable hydrocarbons. Observed differences in product yields and product distributions can be influenced by the change in reaction conditions (temperature, catalyst loading and proper carrier gas). Thus, pyrolysis at the temperature of 450°C, FCC/polymer: 10%(w/w), H_2 and 50 rpm agitator speed appears to be more economically favorable in terms of cost efficient operation and liquid production; however, the optimum process parameters may vary depending on different design objectives.

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