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Using Simulated Distillation or Density to Maximize Lubricants Production from Low Density Polyethylene (LDPE) Pyrolysis

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This work focused on a study to evaluate the potential of using simulated distillation or density data of products obtained from waste Low Density Polyethylene (LDPE) pyrolysis experiments to estimate the influence of process variables in order to maximize lubricant base oils and waxes production, which are in a distillation range above 300 ºC. A laboratory apparatus was built and a two-level full factorial design with three factors (feedstock mass, inert gas flow and temperature) was proposed. The residence time of the LDPE feed was also recorded and included in the statistical analysis. Lubricants and waxes yields in the range 40-70 % wt were obtained. The products were analyzed by SFC, NMR and IR. The statistical analysis of the results showed that temperature, inert gas flow and their interaction have statistical significance in the model an there is no lack of fit. A comparison between the analysis with simulated distillation and density data was performed and it was noticed that density can be used to optimize the reaction section, allowing the maximization of lubricants and waxes production. These results support future application of density as a monitoring parameter of the pyrolysis conversion, since its measuring method is faster and cheaper.

1. Introduction

Plastic was synthesized in 1862, by Alexander Parkes, and represented an industrial phenomenon due its lightness and durability. The package industry is the main consumer (Borsodi et al., 2011). The average annual consumption of plastics is even being used as countries development index and only percentages at about 20 % of the plastic waste are recycled. The plastic conversion into oils has been investigated (Koç and Bigelsu, 2007). In general, there is more interest in converting plastics into fuels, due to the world greater amount production. But in this paper the purpose is to obtain oils in the distillation range (above 300 ºC) of the most valuable products: lubricants base oils and waxes. Those are produced by petroleum refining. Waxes are mainly a byproduct of solvent route, which produces group I lubricants base oils. In Brazil, there is a lack of production and quality of lubricants base oils. In the global scenario of the waxes market, the trend is to supply reduction because of the base oils production route change to hydrorefining. It is also important to mention that plastics don't have an extremely complex composition as petroleum and the products of the suggested conversion can be cleaner and show superior quality, with low SAPs (Sulfur-Ashes-Phosphorus). This work investigated the feasibility of low density polyethylene (LDPE) conversion into waxes and oils, whose distillation range is above 300 °C, by a proposed route. The possibility of conversion section optimization was

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observed through density and simulated distillation analysis by statistical tools. The data obtained by the two properties were correlated in order to reduce time and cost in future researches.

2. Fundamentals

2.1 Feedstock

Base oils are used in the finished lubricants formulation and their quality depends on the composition. Their main features are: viscosity index (higher is better), pour point (the lower the better) and oxidation stability. In this context, the importance of the compounds presence in base oil is as follows: aromatics < polinaphtenics mononaphtenics < n-paraffins <isoparaffins. The feedstock chosen for the tests was a plastic made by LDPE, supplied by White Martins, sectioned as squares (1x1 cm). The reasons for the use of this resin are: large application in package industry and the easiness of collection after consumption; the large amount of polyethylene resins presents in plastic waste (Koç and Bilgesu, 2007; Miskolczi et al., 2003); the chains branch degree (Martinez et al., 2011), important for base oils because it could avoid a step of an expensive hydroisomerization,; the easiness of thermal breakage (Miskolczi et al., 2003) and thus lower power consumption; the absence of contaminants such as sulphur, nitrogen and metals (Miskolczi et al., 2003) that impacts lubricants oxidation stabilities; under optimum conditions, polyethylene pyrolysis usually produces more alkanes and less aromatics than other polymers (Koç and Bilgesu, 2007) and there are no reports of environmental problems under controlled pyrolysis (Kaminsky et al., 2004).

2.2 Experimental Apparatus

The experimental apparatus is shown in Figure 1.

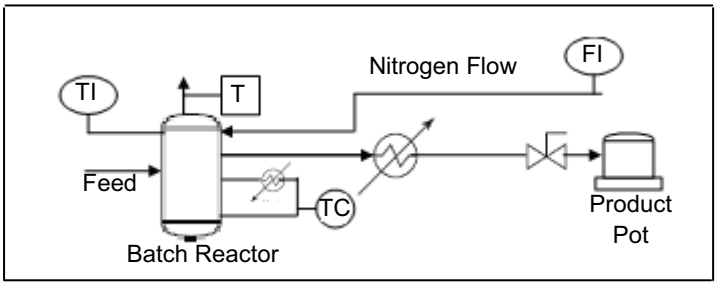

Figure 1. Pyrolysis reaction system (TI – temperature indicator; TC – temperature controller; FI – flow indicator; T – trap)

This step of the research involved only the conversion section. Pyrolysis experimental apparatus comprises: a 1 liter glass reactor coupled to a condensing system with a collection pot, a heating mantled coupled to a temperature controller, and gases absorption traps. The batch glass reactor with the feedstock is inserted in the heating system that promotes melting at about 120 °C and chains degradation. The vapours are carried to the condensation system and the liquids and solids formed are collected in the vessel. Pyrolysis operational parameters to produce mainly linear or branched alkanes were: 400-500 °C temperature range (Koç and Bilgesu, 2007); pressure, controlled by an inert flow that removes products of the reaction zone and reduces side reactions of cracking and coke formation (Miskolczi et al., 2003); absence of catalysts, because they tend to produce larger amount of fractions with boiling points below the specification of the end point of diesel (360 °C) (Na et al., 2006).

2.3 Pyrolysis Experimental Design

Some operational conditions were used to study their influence on the lubricants fraction maximization. At this first moment, the reaction time influence was disregarded and was only recorded for future studies. The end of reaction was defined as the time when no more gas evolution was observed in the reaction section. A full factorial experimental design 2^3 was applied to this case. The three factors varied at two levels are identified in Table 1. The response was yield of the desired fraction estimated

by simulated distillation carried as the standard ASTM D2887 (ASTM, 2012) or density, taking into account that higher densities usually involve products with higher amounts of heavier fractions.
Eight tests were conducted in duplicate, as authentic repetitions and randomized to avoid the distortions in the statistical results. Density analysis is based on ASTM 4052 (ASTM, 2012) and was carried in an automatic densimeter DMA 4500 from Anthon Paar. Simulated distillation was performed in a Hewllett-Packard HP6890 gas chromatograph.

Table 1: Identification factors levels of the experimental design

Code	Factors	Minimum	Maximum
(1)	Temperature (ºC)	470	500
(2)	Nitrogen flow (mL/min)	21	573
(3)	Feedstock mass (g)	100	200

3. Results and Discussion

Density and yield of waxes and oils in a distillation range above 300 ºC estimated by simulated distillation of the whole products data obtained in the tests were used in a statistical study performed with Statistica software release 8. It was possible to evaluate the effects of the variables. Variance analysis (ANOVA) of data was also performed to determine the significant effects and to estimate the variability for the experiments conducted, verifying if there was lack of fit for the models.

3.1 Simulated Distillation

The yield of cut with boiling point above 300 ºC was from 40 % to 70 % wt, showing that it is possible to optimize operational conditions to maximize lubricants and waxes distillation range. In Figure 2 it can be seen simulated distillation curves for three pairs of tests and their good repeatability. The statistical analysis revealed that temperature, nitrogen flow and feedstock mass were not correlated. In Table 2, p-level value below 0.05 warrants, with a 95 % confidence level, that one factor influences the response variable analyzed. So, with errors less than 3 %, it can be deduced that the influence of feedstock mass does not show statistical significance, but temperature, nitrogen flow and their interaction do.

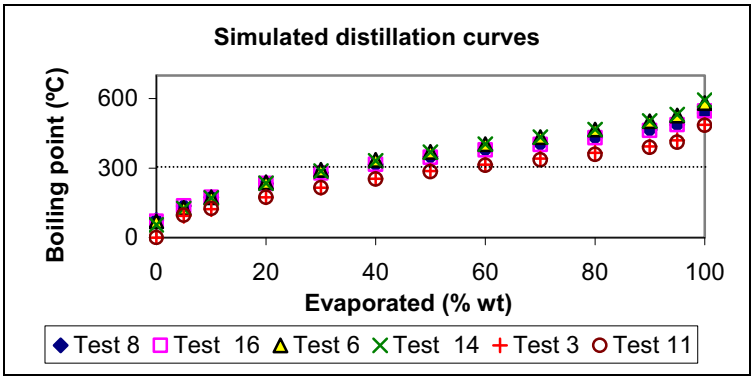

Figure 2: Pairs of curves for correlated experiments.

Furthermore, when the system temperature is raised from 470 to 500 ºC, the yield of desired fractions may increase from 5.26 to 12.62, and when the nitrogen flow is changed from 21 to 573 mL/min, the yield can be raised from 8.31 to 15.67 with a 95 % confidence level.
Since there is interaction between the two variables mentioned, contour lines analysis showed that yields larger than 65 % wt occur in the higher temperatures and nitrogen flows conditions during

pyrolysis. ANOVA is presented in Table 3. In this case, the results were the same of the previous analysis and there was not lack of fit. The model showed a good correlation coefficient of 0.9554.

Table 2: Effects calculation by statistical analysis of simulated distillation data

				Confidence Level	
	Effect	Standard Error	p-level	-95 %	+95 %
Mean	59.42	0.82	0.00	57.56	61.26
(1) Temperature (ºC)	8.94	1.63	0.00	5.26	12.62
(2) N2 flow (mL/min)	11.99	1.63	0.00	8.31	15.67
(3) Mass (g)	2.01	1.63	0.25	-1.67	5.69
(1) by (2)	-4.56	1.63	0.02	-8.24	-0.88
(1) by (3)	-0.89	1.63	0.60	-4.57	2.79
(2) by (3)	-0.84	1.63	0.62	-4.52	2.84
(1) by (2) by (3)	-0.19	1.73	0.92	-4.16	3.79

Table 3: ANOVA for yield of fractions with boiling points above 300 ºC

	Quadratic Sum	Freedom Degree	Quadratic Mean	F	p-level
(1) Temperature (ºC)	319.52	1	319.52	26.85	0.00
(2) N2 Flow (mL/min)	574.80	1	574.80	48.31	0.00
(1) by (2)	83.27	1	83.27	6.99	0.03
Lack of fit	22.30	4	5.57	0.47	0.76
Standard Error	95.19	8	11.90		
Total Quadratic Sum	1,095.06	15			

3.2 Density

When density was used as a response, the analysis was similar to previous done with simulated distillation data. It was observed that the heavier the fraction chosen, the higher the density. According to Table 4, feedstock mass and its interaction with other variables were not significant, but nitrogen flow, temperature and their interaction were. With 95 % confidence it can be seen that if the temperature is increased from 470 to 500 °C, density will be from 0.0030 to 0.0091, and raising nitrogen flow can increment the density of the product from 0.0088 to 0.0149.

Table 4: Effects calculation by statistical analysis of density data

				Confidence Level	
	Effect	Standard Error	p-level	-95 %	+95 %
Mean	0.7614	0.0007	0.0000	0.7599	0.7630
(1) Temperature (ºC)	0.0060	0.0013	0.0019	0.0030	0.0091
(2) N2 flow (mL/min)	0.0119	0.0013	0.0000	0.0088	0.0149
(3) Mass (g)	0.0017	0.0013	0.2311	-0.0013	0.0048
(1) by (2)	-0.0043	0.0013	0.0124	-0.0073	-0.0012
(1) by (3)	-0.0004	0.0013	0.7577	-0.0035	0.0026
(2) by (3)	0.0001	0.0013	0.9564	-0.0030	0.0031
(1) by (2) by (3)	0.0003	0.0013	0.8132	-0.0027	0.0034

Contour lines for this system also demonstrate that highest densities can be obtained with higher temperature and nitrogen flow conditions. Variance Analysis was performed and the correlation coefficient for the model was 0.9582. Regarding the variables significance for the model, it can be said that the results were similar to that for the model with the yield of fractions with distillation range above

300 ºC as the dependent variable. Again, it was observed that there was no lack of fit for the model suggested. In this case, it can be stated that, for future studies, density measure and yield of waxes and oils in a distillation range above 300 ºC estimated from the simulated distillation curve, can be good response variables in order to identify base oils and waxes maximization. This statement is corroborated by the analysis of Figure 3, which corresponds to the chart that relates the average density with the average yield of products with boiling points above 300 ºC, obtained from eight predetermined conditions for the pyrolysis by the experimental design. There is a linear correlation coefficient (R) of 0.9842. It can be also seen the possibility of optimizing the conditions cited, as for the various conditions proposed in the experimental design, it was obtained products with a wide densities range.

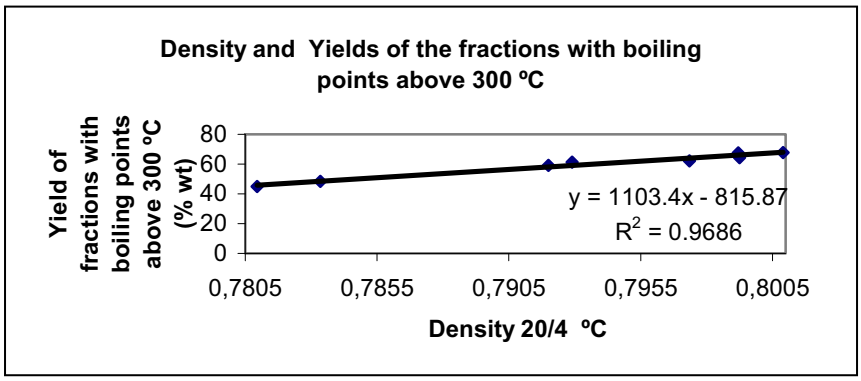

Figure 3: Chart of average density x average yield of products with boiling points above 300 ºC.

3.3 Reaction Time

The reaction time, defined previously, was recorded for each run and the influences of the factors on it were analyzed. Table 5 shows the effects calculated by statistical analysis, considering reaction time as a response variable. In this case, the raise in the temperature from 470 to 500 ºC had a negative effect on the reaction time, decreasing it. The same occurred with higher nitrogen flows values, which accelerated the removal of the vapour phase to the condensation system. Interaction between nitrogen flow and temperature had the positive influence, contributing to increase the intended yield, whereas the other interactions were not statistically significant for the model. Increases of feedstock quantity in the range studied (100-200 g) had a significant effect on reaction time, which was also positive because raises the yield of fractions with boiling points above 300 C.

Table 5: Effects calculation by statistical analysis for reaction time data

				Confidence Level	
	Effect	Standard Error	p-level	-95 %	+95 %
Mean	141.13	4.3962	0.0000	131.18	151.07
(1) Temperature (ºC)	-87.25	8.7924	0.0000	-107.14	-67.36
(2) N2 Flow (mL/min)	-73.25	8.7924	0.0000	-93.14	-53.36
(3) Mass (g)	55.00	8.7924	0.0001	35.11	74.89
(1) by (2)	22.25	8.7924	0.0322	2.36	42.14
(1) by (3)	-12.00	8.7924	0.2055	-31.89	7.89
(2) by (3)	3.00	8.7924	0.7408	-16.89	22.89

The results of variance analysis (ANOVA) are presented in Table 6. The correlation coefficient for this model was 0.9517 and there is no lack of fit.

When the temperature is raised, an increase in cracking is expected, which would lead to products with lower molecular weight. However, in the range studied in this work, 470-500 ºC, the temperature had a positive influence on lubricants and waxes yield.
The influence of the temporal delimitation of the experiment by the definition of a reaction time together with the interactions among temperature, feedstock mass and nitrogen flow, explain this behavior. Therefore, if the feed remained more time in the pyrolysis reactor, it would be more cracked, and more molecules distillation range above 300 ºC would be converted into fuels. Nevertheless, according to the results obtained in this experimental apparatus, when the temperature was raised, the molecules rapidly went from the solid state to vapour state, being further dragged by the nitrogen flow to the condensation section, hence remaining less time in the reaction section, and being less cracked.

Table 6: ANOVA for Reaction Time

	Quadratic Sum	Freedom Degree	Quadratic Mean	F	p-level
(1) Temperature (ºC)	30,450.25	1	30,450.25	98.66	0.0000
(2) N2 Flow (mL/min)	21,462.25	1	21,462.25	69.54	0.0000
(1) by (2)	12,100.00	1	12,100.00	39.20	0.0001
Lack of fit	1,980.25	1	1,980.25	6.42	0.0278
Standard Error	3,395.00	11	308.64		
Total Quadratic Sum	69,387.75	15			

4. Conclusions

This work provided experimental evidence that it is possible to obtain products in the distillation lubricants and waxes range from pyrolysis of plastics made by LDPE. Statistical analysis indicates that for the experimental apparatus and the experimental design developed, nitrogen flow and temperature are the main parameters to be optimized to maximize the desired products. Nevertheless, to control reaction time of the feedstock and also molecule cracking, it is necessary to optimize feed quantity and nitrogen flow. Furthermore, the results show that it is possible to manipulate the chosen input variables of the reaction section aiming product optimization. Simulated distillation and density are variables that can be used as monitoring parameters to infer conversion in the experiment. So, for time and cost savings, this work points out density as the most adequate parameter to monitor and control the tests in future experimental designs.

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