THE INFLUENCE OF THE PYROLYSIS CONDITIONS IN A ROTARY OVEN ON THE CHARACTERISTICS OF THE PRODUCTS

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Abstract

The pyrolysis of 1:1 blends of reinforcing fibre (RF) from tyre wastes with low rank bituminous coal were carried out in a rotary oven. The pyrolysis conditions were modified in order to study their influence on the yield and characteristics of the char and oil obtained. The variables studied were as follows: rotation speed, final pyrolysis temperature, N₂ flow and heating rate. The textural characteristics of the char were studied by means of N₂ adsorption at 77 K, whereas the oil composition was studied by infrared spectroscopy and gas chromatography.

Modification of the variables did not have any effect on the composition or textural properties of RF/Coal char. However, an increase in the nitrogen flow, rotary speed and a decrease in the heating rate led to a higher oil yield with more oxygenated groups and less aromaticity. These conditions also caused an increase in the contribution of the light oil to the oil yield. Moreover, an increment in the final temperature also resulted in a higher percentage of light oil, a greater amount of aromatic compounds and smaller number of oxygenated groups.

Keywords: rotary reactor, reinforcing fibre, coal, tyre waste, pyrolysis.

1. Introduction

The economic and environmental problems associated with the generation of scrap tyres are increasing due to the remarkable growth in the number of vehicles worldwide. For these reasons, the management of used tires represents a serious technological, economic and ecological challenge [1, 2]. In recent years, the combustion, gasification and pyrolysis of wastes derived from tyre rubber have been studied in order to find a use for the huge amount of waste [3-12]. These technologies were considered the most appropriate for exploiting a waste which contains a high amount of carbon and has a high calorific value [13].

Pyrolysis essentially involves the decomposition of the wastes derived from tyre rubber at high temperatures (300–900°C) in an atmosphere of an inert gas such as nitrogen at atmospheric pressure, into three products: gas, pyrolytic oil and char. The composition of each fraction depends on the pyrolysis conditions used and on the composition of the tyre [7]. The main advantage of the process is that it deals with wastes, which would otherwise be difficult to dispose of and creates reusable products.

Pyrolysis has also been referred to as reverse polymerisation, thermal depolymerisation or polymer cracking whose main reactions are dehydration, cracking, isomerisation, dehydrogenation, aromatisation and condensation [14]. Depending on the ultimate objective of the pyrolysis, it is necessary to establish the optimal conditions since the characteristics of the products will depend on the configuration of the oven. Several studies have been performed to investigate the influence of temperature, pressure, heating rate and the residence time of the volatiles and solids on the product yields and characteristics using different types of reactors [14, 15].

Pyrolysis of the tyres has been carried out by means of different experimental procedures, in laboratory and commercial scale plants using autoclaves, rotary kilns, screw conveyors (auger), fixed, spouted, entrained and fluidised beds, rotating cone, vortex reactors, melting vessels, plasma reactors, free-fall, tubing bomb reactors, vacuum pyrolysis and the ablative process, in addition to other techniques. Such studies have been focused on different aspects of the pyrolysis process and the results obtained have then been related to the feedstock, operating conditions used for the experiments, the specific characteristics of the system used: type of reactor, efficiency of heat transfer, etc. [16, 17]

All the reactors/configurations have advantages and disadvantages in terms of technical, economic and ecological parameters and are used for various energy

applications such as generation of heat or electricity and the production of liquid fuels and char.

Rotating drums are extensively used in chemical industries as kilns, mixers, dryers and reactors. The rotary reactor prevents agglomeration and ensures a good mixing of the particles because of the rotation of the reactor.

The aim of the present work is to study the pyrolysis of 1:1 blends of tyre waste reinforcing fibre (RF) with low rank bituminous coal in order to establish the influence of the variables of the rotary reactor on the yields and characteristics of the products.

2. Experimental

The raw materials used for the pyrolysis experiments were fluff/fibres (RF) obtained as a waste during the grinding and shredding of scrap tyres from the processing of car and truck tyres [5,13]; and a low rank coal (Volatile matter = 36.2 wt% db, ash content = 6.4 wt% db) used in blast furnaces for pulverized coal injection.

The pyrolysis experiments in the rotary oven were carried out with a 1:1 blend of the RF and Coal. A constant mass of sample of 40 g was used in all the experiments. A cold trap and a column filled with amberlite resin allowed the recovery of the condensable products, i.e. heavy oil and light oil respectively. The char and liquid product yields were calculated relative to the starting material, while the gas yield was calculated by difference. A diagram showing the configuration of the oven has been published previously [13]. For the pyrolysis experiments the coal was ground to a size smaller than 1.18 mm while RF was used, as received. The variables studied were: three rotation speeds (low=8.2 rpm, high=13.8 rpm and maximum=15.1 rpm); final pyrolysis temperature (850 and 950 °C), nitrogen flow (100, 400 and 600 ml/min) and heating rate (1 and 5 °C/min). The following notation has been used throughout the text: 850-L-400-1 indicates a pyrolysis experiment carried out to a final temperature of 850 °C at a low rotary speed, a N₂ flow of 400 ml/min and a heating rate of 1 °C/min. This experiment was considered as a basis for comparison with the rest. Table 1 shows the conditions used for each experiment.

The chars obtained were characterized by elemental analysis, which was carried out in a LECO CHN-2000 for C, H and N, a LECO S-144 DR for sulphur and a LECO VTF-900 for direct oxygen determination. The ash content was determined by thermogravimetric analysis using a TA Instruments SDT 2960 thermoanalyser.

The textural properties of the chars were studied by means of N₂ adsorption at 77 K on a Micromeritics ASAP 2420 apparatus. The software package provided

with the equipment was used to determine the textural characteristics. The specific surface area (S_{BET}) was calculated by means of the BET method. The total pore volume (V_{T}) was measured at $P/P_0 = 0.97$. The micropore volume was determined by applying the Dubinin equation to the lower relative pressure zone of the N_2 isotherm. The mesoporosity was calculated as the difference between the total pore volume (V_{T}) and the micropore volume.

The elemental composition of the oils was determined using the same procedures as in the case of the chars. The calorific value was measured in an adiabatic IKA – Calorimeter C4000, Analysentechnik Heitersheim apparatus. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet Magna-IR560 spectrometer equipped with a DTGS detector. Gas chromatographic analyses of oils were carried out on an Agilent – 7890A gas chromatograph equipped with flame ionization and mass spectrometry detectors (GC–FID–MS). The separations were performed using a fused-silica capillary column (HP-5MS). The temperature was programmed to rise from 50 to 295 °C at a rate of 4 °C/min, the final temperature being maintained for 20 min. Helium was used as the carrier gas and split ratios of 1:200 and 1:50 were employed in the MS and FID injectors respectively. The quantitative analyses were based on peak area determinations. The data presented are the average of 2 chromatograms.

3. Results and discussion

The mass balances obtained are presented in Figure 1, in four graphs one for each variable studied. From the amount of compounds retained in the amberlite resin, the contribution of the light oil to the oil yield was determined and shown in Figure 2. The char yield does not appear to be greatly affected by the variables studied and in all cases it is around 48 ± 1 wt%, and therefore the main product of the pyrolysis. S.Q. Li et al [18] and S. Galvagno et al [19] also found that the solid char yield remained essentially constant when the final temperature was modified using a continuous rotary kiln. However, other authors using a fluidised bed reactor and a conical spouted bed reactor found that the solid fraction increased at higher temperatures [20, 21]. After the char, gas is the second most abundant pyrolysis product. Unlike the char yields, the yields of gas and oil were more influenced by the pyrolysis conditions. **The rotary speed** had little effect on the oil and gas yield. It appears that as the speed increases the oil yield increases while that of gas decreases. This result can be attributed to the fact that an increase in the speed contributes to the exit of volatiles from the hot zone of the reactor, preventing the occurrence of secondary reactions. Secondary reactions would result in lower oil and higher gas yields. The

increase in the **final pyrolysis temperature** produces only a very slight variation in the yield of char, gas and oil. Nevertheless the type of compounds present in the oil must be different considering that at 950 °C the percentage of light oil increases. The higher residence time of the condensable gases in the hot zone of the reactor in the case of the experiment carried out at 950 °C will cause some larger compounds to undergo cracking reactions which will produce smaller compounds with a consequent increase in the percentage of light oil. S.Q. Li et al [18] using a rotary kiln also reported an increase in the oil light fraction when the temperature increased.

The variation in the **N₂ flow** had the greatest effect on the mass balances as shown in Figure 1. The char and gas yields increased when the nitrogen flow decreased, whereas the oil yield decreased. These results are due to the residence time in the hot zone of the reactor. As the residence time increases, the oil undergoes more cracking and condensation reactions that give rise to higher gas and char yields. A high N₂ flow implies that the pyrolysis gases are swept from the reactor quickly and therefore secondary reactions are avoided. The same reasoning explains why the amount of light oil is lower when the N₂ flow is slower (Figure 2).

When the **heating rate** decreased no modification in the char yield was observed whereas the oil yield was higher and the gas yield lower. A slow heating rate implies that the rate of volatile matter evolution will also be lower. Consequently as volatiles are produced they will be swept out easily and condense, giving rise to a higher yield of oil. In addition the amount of light oil will also increase at a heating rate of 1 °C/min (Figure 2). The degradation rate increased as the heating rate increased resulting in an increase in the amount of volatiles. These volatiles may have been subject to secondary reactions with the consequent increase in the gas fraction as in the study carried out in a fixed bed reactor (FBR) by Gonzalez et al [7]. However, whereas R. Murillo et al [4] did not observe a remarkable influence on the total tyre conversion in their FBR, P.T. Williams et al. [22] found that increasing the heating rate caused a decrease in char yield and an increase in the liquid and gas yields. The effect of heating rate on tyre pyrolysis can show different behaviours, caused by secondary reactions related to the residence time of the volatiles in the high temperature zone of the reactor.

In summary the oil yield and its light fraction increased as the N₂ flow increased and the heating rate decreased. The rotary speed and final pyrolysis temperature (in the range studied) did not produce any major changes in the mass balance but the light oil fraction increased with the rise in final temperature.

The chars were characterized by means of immediate and elemental analysis (Table 2) and N₂ adsorption at 77 K (Table 3).

The elemental composition of all the chars produced was very similar even in the case of variation of the N_2 flow, the variable that produces the greatest modifications in the mass balances. Only the ash content at the highest N_2 flow is at its maximum. The ash and carbon contents were around 9.4 ± 1.5 % and 87.6 ± 1.6 % respectively.

The nitrogen isotherms obtained show that these materials are mesoporous with a low BET surface area and total volume (Table 3), the mesopore volume accounting for at least 88 % of the total pore volume.

In all the experiments the heavy oil fraction constitutes more than 78 % of the oil yield. The elemental analysis of these oils is shown in Table 4. As in the case of the chars all the oils have a similar composition and a similar calorific value because of the C content [23]. The C content is high, around 79.3 ± 0.8 wt %, as are the calorific values, around 8609 ± 197 (kcal/kg). The oils produced from the pyrolysis of tyre wastes and those from their co-pyrolysis with coal are comparable to the HHVs of other fuels [6, 15, 24-27]. The greatest differences were obtained when the N_2 flow or the heating rate were modified.

A decrease in the **N_2 flow** is accompanied by a change in the elemental oil composition because the percentage of H and O decreases. This indicates that fewer saturated and oxygenated compounds are present in the oil, as is confirmed by the increase in the C/H atomic ratio.

In the case of the **heating rate**, when heating rate was 5 °C/min, the oil contained less carbon and hydrogen, and more nitrogen, sulphur and oxygen than at 1 °C/min.

The oil yield obtained at the different **final temperatures** was the same, but its composition was different. The light oil yield at high temperature was greater because of the existence of cracking reactions. For the same reason oxygenated compounds produced SO_2 , NO_x , CO_2 and CO [28] and as a consequence the oil had less oxygen.

Moreover, light and heavy oils were characterized by Fourier transform infrared spectroscopy (FTIR) and gas chromatography (GC-FID-MS).

Figure 3 shows FTIR spectra corresponding to light and heavy oils. In all the spectra, aliphatic groups are more numerous than aromatic ones, although the heavy oils have stronger bands in the range assigned to aromatic compounds. In addition the spectra corresponding to heavy oils present strong bands in the $900-700\text{ cm}^{-1}$ range which is associated to aromatic C-H out-of-plane deformation (see Figure 3B).

All the spectra have a small peak at 2230 cm^{-1} which corresponds to a $C\equiv N$ bond associated to compounds such as benzonitrile and its derivatives that appear

due to the decomposition of Nylon present in RF [5, 15, 29]. The band at 1600 cm^{-1} , which corresponds to aromatic C=C is present in all the spectra together with the bands at 1455 and 1375 cm^{-1} that correspond to bending vibrations of methylene and methyl groups [22, 29,30].

FTIR allows not only a qualitative analysis but also a semi-quantitative analysis that is based on the area of the absorption bands at specific wavenumbers in the spectra. For this purpose various indices can be calculated using the integrated area (A) of different absorption bands of the FTIR spectra. Although indices derived from FTIR spectra have been used to evaluate the chemical characteristics of fuels [31-33], only two have been employed in the present research work: 1. Degree of aromaticity and 2. Ratio of oxygenated functional groups.

The degree of aromaticity ($A_{\text{C-H aromatic}}/A_{\text{C-H aliphatic}}$) was calculated from the ratio of the area in the $3100\text{--}2990\text{ cm}^{-1}$ region corresponding to aromatic C-H versus the area in the $2990\text{--}2795\text{ cm}^{-1}$ region, corresponding to aliphatic C-H (CH, CH₂ and CH₃). The amount of oxygenated functional groups can be determined using the index calculated from the ratio of the area in the $1770\text{--}1650\text{ cm}^{-1}$ range versus the area of the band at 1600 cm^{-1} which corresponds to the stretching of the C=C bond in aromatic compounds.

Figure 4 shows the variation of these indices calculated for light and heavy oil when the pyrolysis conditions are modified.

The **N₂ flow and heating rate** are the two variables that produce the greatest modification in the FTIR indices. The aromaticity index increases with the decrease in N₂ flow for light and heavy oils, which is in agreement with the longer residence time of the volatiles in the reactor at a low N₂ flow. This also agrees with their higher C/H ratio (Table 4). The degree of aromaticity was not influenced by modifications in the rotation speed and final pyrolysis temperature. The values obtained for this index are lower than 0.2 which indicates that aromatic compounds are less abundant than aliphatic compounds. The lower heating rate produced less aromaticity in the oils and compounds with more oxygenated functional groups. These results are in agreement with the hypothesis that a lower heating rate causes a slower evolution of volatiles which are consequently more easily expelled from the reactor. In this way secondary reactions which increase aromaticity and decrease the number of oxygen groups are avoided.

An increase in the **final pyrolysis temperature** produces oils with a lower oxygen content due to the existence of cracking reactions. These reactions produce light oxygenated compounds that evolve as non-condensable gases. The FTIR results agree well with the aforementioned reaction mechanisms that indicate that

increasing temperature produces the cracking of volatile products and a more pronounced aromatization of the pyrolytic oil [18].

The dichloromethane (DCM) soluble part of pyrolysis oils was analyzed by means of gas chromatography with a view to identifying the compounds present as a function of the experimental conditions. Figures 5 and 6 show GC-FID chromatograms corresponding to the light and heavy oils, respectively, produced at different N₂ flows and rotation speeds. Peak identification has been included in the caption. Generally the compounds that appear in all the samples are the same, although their concentrations are different, as reflected by the height of the peaks. As explained above the distribution between light and heavy oil depends on the pyrolysis conditions. Light oil represents a higher percentage of the total oil when the residence time of the condensable gases inside the hot zone of the reactor is lower or when these gases remain up to a higher temperature (Figure 2). The light oil may have resulted from the direct decomposition of the samples or from secondary reactions of condensable gases due to their longer residence time inside the hot zone of the reactor. The main compounds present in the light oil for a N₂ flow of 100 ml/min (850-L-100-5) are toluene (peak 1), cyclopentanone (Peak 2), xylene (peak 4) and ethenylethylbenzene (peaks 10, 11). These compounds can be produced either by primary decomposition reactions, or by secondary cracking reactions in which light compounds are obtained from the break-up of larger structures. In the present study when the N₂ flow increased, the time spent in the hot zone of the oven decreased and, fewer secondary reactions were produced in fewer products from secondary reactions in the light oil. The number of compounds resulting from direct decomposition increased, like limonene (peak 9) and benzonitrile (peak 7). It can be inferred therefore, that when the N₂ flow increased from 100 to 600 ml/min the limonene and benzonitrile peaks were getting higher, while the toluene, xylene and ethenyl-ethyl-benzene peaks were getting smaller.

A similar behaviour occurred when the rotary speed was increased. A comparison of the chromatograms corresponding to low (Figure 5, 850-L-400-5) and maximum rotary speed (Figure 5, 850-M-400-5) shows that peaks 7 and 9 corresponding to limonene and benzonitrile, both derived from direct decomposition of RF, were higher in the sample obtained at maximum speed. On the other hand toluene (peak 1), cyclopentanone (peak 2), xylene (peak 4) and ethenyl-ethyl-benzene (peak 6) were smaller. The reason for this is that the oil from the sample obtained at the lowest rotary speed spent more time in the hot zone of the oven which implies that the oil was subjected to secondary reactions.

The light oils obtained at different final temperatures and heating rates were very similar to that obtained under standard conditions i.e. 850-L-400-5. These samples were mainly composed of toluene, cyclopentanone, ethyl-benzene, xylene, styrene, benzonitrile, limonene and ethenyl-ethyl-benzene. Other authors employing a rotary kiln have found that increasing temperature from 450 to 600°C was accompanied by an increase in the concentration of the BTX fraction. However, the BTX concentration decreased when working at temperatures higher than 600°C since Diels-Alder aromatization occurred giving rise to higher levels of PAHs. The BTX fraction of the light oils obtained at different final temperatures in the present research work was similar since the temperatures were too high to appreciate the difference [18]. On the other hand the heavy oil obtained at the lowest N₂ flow (i.e. 100 ml/min) has the most differences in its composition. It also has the highest concentration of aromatics such as naphthalene (peak 7), methyl-naphthalene (peak 11), phenanthrene (peak 18) or fluoranthene (peak 23). These differences are due to the longer residence time of the decomposition products in the hot zone of the reactor resulting in secondary reactions like that of Diels–Alder and condensation [25, 22, 34-36].

Significant peaks are also apparent in the heavy oil chromatograms corresponding to benzoic acid and caprolactam obtained from the decomposition of the polymers in RF. The influence of coal can also be seen in the series of aliphatic compounds from C18 to C30 [15].

It was not our objective to make a detailed quantification of the volatile compounds that were present in the heavy oil but to define the chromatographic regions that are delimited by the boiling point intervals and molecular masses. Three chromatographic regions were defined. The first region R1 comprises compounds that eluted between benzonitrile, (tr=5 min, b.p.=188 °C, MW=103 g/mol) and naphthalene (tr=13.39 min, b.p.= 218 °C, MW=128); the second, R2, includes the compounds that eluted between naphthalene and phenanthrene/anthracene (tr=31.20 min, b.p.=337 °C, MW=178) and the third one, R3, comprises those that eluted between phenanthrene/anthracene and the end of the chromatogram (tr=60 min). Figure 7 shows the percentage of each region for each set of pyrolysis conditions. The distribution of the compounds present in the heavy oil depends on the pyrolysis conditions although in all the cases studied the highest percentage corresponds to R2 that contains aromatic compounds such as naphthalene and its derivatives together with compounds obtained from the decomposition of the polymers in RF such as caprolactam, benzoic acid. Most of the compounds present in R3 were derived from the direct decomposition of the raw materials. Consequently

the highest percentages in this region were obtained when the pyrolysis conditions involved less cracking. This region is composed mainly of long chain aliphatics. The highest percentages were obtained at the maximum rotation speed, the highest N₂ flow and the lowest heating rate.

Limonene was chosen out of the compounds present in the light oil in order to study its concentration under different pyrolysis conditions (Table 5). It is a terpene that is produced from the decomposition of rubber present in RF [5]. High temperatures or the occurrence of secondary reactions in the pyrolysis system tend to decrease its concentration. The results in Table 5 show that the concentration of limonene doubled from 11 to 22 % when the rotary speed was increased. Similarly an increase in the N₂ flow produced an increase in limonene from 1 to 19 %. However an increase in the final pyrolysis temperature from 850 to 950 °C and heating rate did not produce any significant change in the concentration of limonene

In order to facilitate comparison between the compositions of the heavy oils produced two indices were calculated on the basis of the percentages of various types of compounds present in the oils. Table 5 shows the amount of long chain aliphatic compounds (C₂₁-C₃₀) and a substitution index calculated from the ratio trimethyl-naphthalene to naphthalene.

It can be seen that the amount of aliphatics (C₂₁-C₃₀) increased as the rotary speed and N₂ flow rose, and the heating rate fell. Final temperature did not have any influence on the percentage of C₂₁-C₃₀. However, the final temperature did affect the substitution index which increased in the oils obtained at a higher N₂ flow and lower final temperature. The rotation speed and heating rate did not have any effect.

4. Conclusions

Modification of the variables in this rotary reactor did not have an influence on the yield composition or textural properties of the RF/Coal char produced in this study. On the other hand increasing the N₂ flow, rotary speed and decreasing the heating rate produced a higher oil yield and a higher percentage of light oil. An increase in the final temperature also led to a higher light oil yield.

When the rotary speed and N₂ flow was increased, the resulting oil contained more oxygenated groups, less aromaticity and most of the compounds present in the oil resulted from direct decomposition as limonene, benzonitrile or long aliphatic chains. When the final pyrolysis temperature or heating rate was increased, the oil became more aromatic with fewer oxygenated groups.

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Table1. Experimental pyrolysis conditions.

Pyrolysis conditions	Final pyrolysis temperature (°C)	Rotary speed	Nitrogen flow (ml/min)	Heating rate (°C/min)
850-L-400-5	850	Low	400	5
850-H-400-5	850	High	400	5
850-M-400-5	850	Maximum	400	5
950-L-400-5	950	Low	400	5
850-L-600-5	850	Low	600	5
850-L-100-5	850	Low	100	5
850-L-400-1	850	Low	400	1

Table 2. Proximate and elemental analysis of the chars.

Pyrolysis conditions	Ash (wt.% db)	MV* (db)	C (wt.% db)	H (wt.% db)	N (wt.% db)	S (wt.% db)	O (wt.% db)
850-L-400-5	8.0	3.9	88.1	1.0	1.7	1.01	3.8
850-H-400-5	9.9	3.0	86.5	0.9	1.8	0.85	2.1
850-M-400-5	9.9	2.7	88.6	0.9	1.8	0.84	1.4
950-L-400-5	8.2	2.5	89.6	0.6	1.7	0.89	0.8
850-L-600-5	12.1	3.1	85.2	0.9	1.7	0.99	1.8
850-L-100-5	9.3	2.9	86.3	0.9	1.6	0.95	1.5
850-L-400-1	8.2	3.0	88.6	0.8	1.9	0.84	1.3

*: Volatile matter content.

Table 3. Textural characteristics of chars from N₂ isotherms at 77K.

Sample	S _{BET} (m ² /g)	V _{Total} (mm ³ /g)	V _{micropores} (mm ³ /g)	V _{mesopores} (mm ³ /g)
850-L-400-5	11	40	4	36
850-H-400-5	9	36	4	32
850-M-400-5	10	38	4	34
950-L-400-5	10	39	4	35
850-L-600-5	10	36	4	32
850-L-100-5	6	32	2	30
850-L-400-1	11	43	4	39

Table 4. Elemental analysis of oils obtained from pyrolysis.

Tar Sample	C (wt.% db)	H (wt.% db)	N (wt.% db)	S (wt.% db)	O* (wt.% db)	C/H**	HHV (kcal/kg)	LHV (kcal/kg)
850-L-400-5	78.5	8.1	2.8	1.0	9.6	0.8	8698	8303
850-H-400-5	80.3	8.6	2.2	0.8	8.1	0.8	8566	8145
850-M-400-5	78.6	8.4	2.5	0.8	9.7	0.8	8481	8070
950-L-400-5	79.2	8.2	2.3	0.9	9.4	0.8	8632	8229
850-L-600-5	78.6	8.9	2.0	0.8	9.7	0.7	8335	7899
850-L-100-5	79.4	7.5	2.5	1.2	9.4	0.9	8579	8212
850-L-400-1	80.6	8.9	1.9	0.8	7.8	0.8	8970	8533

*: Oxygen content by difference. **: C/H atomic ratio.

Table 5. Indices calculated from the chromatographic analysis.

	Light oil	Heavy oil	
	Limonene (%)	C21-C30 (%)	Substitution index*
850-L-400-5	11	9	2.3
850-H-400-5	13	13	2.0
850-M-400-5	22	14	2.1
950-L-400-5	11	9	1.2
850-L-600-5	19	13	2.5
850-L-100-5	1	5	0.4
850-L-400-1	10	13	2.2

*: Thimethylnaphthalene/naphthalene

Figure 1. Mass balance of the pyrolysis experiments with different conditions.

Figure 2. Distribution between heavy oil and light oil depending on the pyrolysis conditions.

Figure 3. FTIR spectra of oil a) Light oil, b) Heavy oil.

Figure 4. Ratios of integrated absorption bands calculated from the FTIR spectra of light and heavy oils.

Figure 5. Capillary gas chromatograms of light oil. Peak identification: 1. Toluene, 2. Ciclopentanone, 3. Ethylbenzene, 4. Xylene, 5. Styrene, 6. Ethylmethylbenzene, 7. Benzonitrile, 8. Trimethylbenzene, 9. Limonene, 10. Ethenylethylbenzene, 11. Methylphenol, 12. Methylbenzonitrile, 13. Methylindene.

Figure 6. Capillary gas chromatograms of heavy oil. Peak identification: 1. Benzonitrile, 2. Phenol, 3. Methylphenol, 4. Methylphenol, 5. Methylbenzonitrile, 6. Dimethylphenol, 7. Naphthalene, 8. Benzothiazole, 9. Benzoic acid, 10. Caprolactame, 11. Methylnaphthalene, 12. Biphenyl, 13. Dimethylnaphthalene, 14. Acenaphthalene, 15. Trimethylnaphthalene, 16. Fluorene, 17. Methylfluorene, 18. Phenantrene, 19. C18, 20. Hexilbemzamida, 21. Methylphenantrene, 22. C20, 23. Fluoranthene, 24. C21 – C30.

Figure 7. Percentage of compounds that elute in different chromatographic regions.