

Hydrogen or Soot?: Partial Oxidation of High-boiling Hydrocarbon Wastes

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This paper is focused on researching the influence of process parameters of partial oxidation, such as quality of hydrocarbon raw materials that differ in their stock properties (especially boiling point and viscosity) on the composition of output gas (selectivity of the process), and also on the formation extent of soot which could be used as an excellent and valued sorbent CHEZACARB® and/or filler in the rubber industry, e.g. for automotive tires. The effects of steam flow rate and the oxygen to raw material feed rate ratio is discussed as well. In addition, sensitivity of POX product composition depending on properties of different raw materials and reaction conditions were analysed in this study.

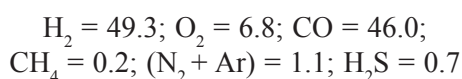
Key words:

partial oxidation, waste, hydrocarbon, hydrogen, soot

Introduction

An increased demand on hydrogen, which is essential for a deeper hydrotreating of petroleum oils to ensure better quality of motor fuels (from the point of view of exhaust emissions) motivate research on partial oxidation (POX) of high-boiling hydrocarbons residues or alternative biomass waste^{1–4}. Process POX is based on the reaction between raw material and oxygen in the presence of water vapour^{5–10} and its selectivity with regard both to composition of the exhaust gas and soot formation and strongly depends on lambda parameter representing molar ratio of oxygen to carbon content in raw material fed to the POX reactor. Combination of thermal pyrolysis of raw material to hydrogen, soot, methane and oxidation or imperfect combustion of wastes to carbon dioxide, carbon monoxide, water are parallel reactions in the reaction space.

The raw material is gasified in industrial plants⁵ typically at temperatures above 1300 °C under pressure of 3.5 MPa. The performance of the operating unit enables production (in the reaction space of 1 m³) of 1500 m³ h⁻¹ of synthesis gas of a typical composition (% vol.):



An impact steam and oxygen ratio to the feed on the selectivity of the partial oxidation of high-boiling hydrocarbons with regard to the composition of the exhaust gas was detected in our previous studies^{1,2}. Content of components in a gaseous product was in very good conformity with a synthesis gas composition produced by the plant unit of UNIPETROL RPA Co., which operates according to the license of Shell Co⁵. Significant formation of carbon black – soot – as a by-product of partial oxidation under the process conditions has to be separated^{6–10}. Its production can be monitored by discharging a soot dispersion into water, which arises at product quench cooling by water after outlet from the POX reactor. The impact of both steam and oxygen ratio to hydrocarbon oils feed on selectivity of its partial oxidation (POX) of black and white oils with regard to the composition of gaseous product was investigated in this study. Process performance is compared with results of simulation by Aspen Plus program. Both chemical equilibrium and kinetics of pyrolysis and soot formation are taken into account.

Experimental

Raw materials

The pilot unit POX tests were conducted at temperature 1150 – 1200 °C and under nearly ambient pressure (0.11 MPa) with the following materials: Black oil (mazut), white oil (base oil Mogul HC

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Table 1 – Elemental composition of raw materials

[% wt.]	C	H	S	N	Ni	Fe	Total
Mazut	85.99	10.93	2.6	0.45	0.003125	0.00351	99.98
Mogul HC-68	86.37	13.55	0.000161	<0.00003	0.00004	0.00006	99.92
Mogul HC-68 + Ni	86.25	13.50	0.000306	<0.00005	0.03640	0.00013	99.79

68) and white oil with nickel (*II*) acetylacetonate (0.16 % wt.). All these materials were analyzed for kinematic viscosity (1348 and 56 mm² s⁻¹ at 40 °C, resp.), density (963 and 869 kg m⁻³ at 20 °C, resp.) and elemental composition, see Table 1. Special attention was paid also to a catalytic effect of the nickel concentration in the base oil Mogul HC68 POX on product composition.

Apparatus

The pilot plant unit used in this study was described in our previous papers^{1,2}. Cylindrical reactor for partial oxidation of hydrocarbons was implemented using a heat-resistant internal lining (thermal insulation layer made of aluminosilicate-based ceramics) with auxiliary electrical heating system (furnished by five modules of 3 kW), compensating for a significant part of heat loss from the reaction space. The inside of the reactor had a height of 1.8 m and a diameter of 0.3 m. The temperature along the internal reactor wall was monitored in three positions and from the thermometers response the mean reaction temperature was determined on line. Water chilled co-annular nozzle for the supply of raw material, oxygen and steam was located in the upper lid of the reactor – see Figure 1. Raw hydrocarbon mixture and demineralised water for a steam generator were fed by precise calibrated piston-pumps. The pressure inside the reactor was controlled at the level of 1.4 kPa above ambient.

The reaction product was quenched, cooled down and washed with water. The produced gas mixture was regularly sampled and analyzed by GC method and subsequently introduced into a furnace



Fig. 1 – Nozzle of pilot plant reactor before (left) and after (right) experimental test

for the disposal of flammable hydrogen and carbon monoxide from the unit. Digital parameters measurement and apparatus control were performed by data acquisition system using WinControl 2005 software. Based on GC analysis, reactor steady state achieving was monitored. After reaching steady state, three independent samples were subsequently taken in order to increase accuracy of measurement.

The data were used to determine the mean reaction product composition. In addition, samples of soot dispersion in water were collected for subsequent analysis of the soot properties. A microphotography example of typical primary soot particles is shown in Figure 2. The texture characteristics, specific surface area S_{BET} and micropores volume V_{micro} were measured (by N₂ sorption) using ASAP 2010 M, Micromeritics, Co., USA.

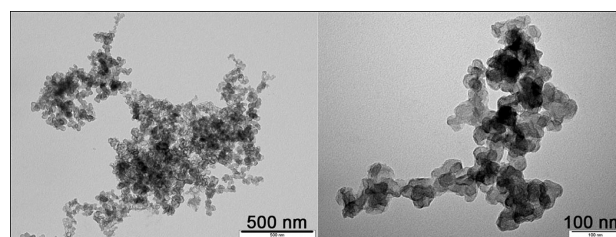


Fig. 2 – Example of primary soot particles structure (Chezacarb[®])⁸

Results and discussion

The raw materials feed rates, oxygen and steam flow rates during experimental partial oxidation tests in the pilot plant unit are summarized in Table 2. Typical mean temperature in reactor was controlled within the interval of 1150–1200 °C and nearly ambient pressure was applied (0.11 MPa).

The effect of steam feed on partial oxidation selectivity has not been investigated in this paper because of the limited number of experiments. This topic was discussed in our previous study² where the reciprocal effect of steam feed on mean temperature in reactor has been described. It is evident that the higher steam flow rate makes the lower partial pressure of hydrocarbons and oxygen. Also, shorter residence time of reaction components in the reactor should be supposed. In such a situation,

Table 2 – Parameters of experimental tests

Test	Raw material	Feed [kg h ⁻¹]	O ₂ [kg h ⁻¹]	Steam [kg h ⁻¹]
1	White oil Mogul HC 68	1.50	2.32	1.00
2	White oil Mogul HC 68	1.50	1.50	1.00
3	Black oil – Mazut	1.58	1.50	1.00
4	Black oil – Mazut	1.98	1.90	0.62
5	Black oil – Mazut	1.58	1.28	1.51
6	Black oil – Mazut	1.57	1.76	1.00
7	Black oil – Mazut	2.52	1.25	1.52
8	Black oil – Mazut	1.98	1.60	1.22
9	Mogul HC 68 + Ni	1.57	1.50	1.00

the mean specific heat of reaction mixture is changed as well. These common effects have an impact on product composition, e.g. the higher steam feed rate supports “water shift” reaction of carbon monoxide to carbon dioxide and hydrogen.

Comparison of raw materials

The first point investigated during pilot plant tests was the effect of physicochemical properties and elemental composition of raw material on selectivity of the partial oxidation process. Black oil (mazut) and white oil (base white oil Mogul HC 68) differ mainly in boiling point, viscosity, and also in content of impurities (e.g. nickel). Figure 3 presents the effect of the raw material on gaseous product composition, i.e. main components – hydrogen, carbon oxides, methane, ethane & ethylene, sulphane and also non-reacted oxygen (water vapour was not detected). It is evident that the contents of the com-

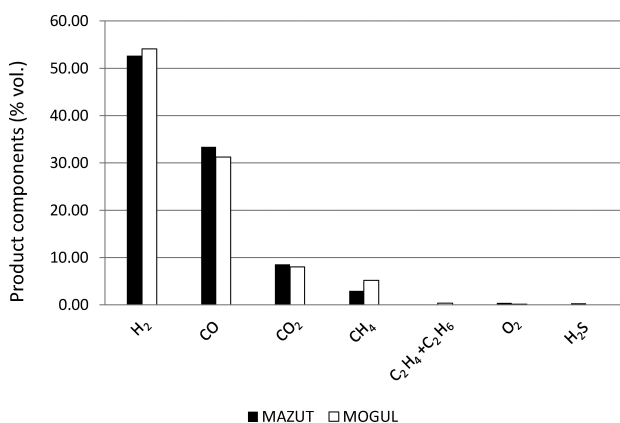


Fig. 3 – Comparison of gaseous product composition, from black and white oils partial oxidation; feed rate 1.58 and 1.5 kg h⁻¹, oxygen 1.5 kg h⁻¹, steam 1.0 kg h⁻¹; tests 2 and 3

ponents are very close to each other in the case of compared tests 2 and 3.

Effect of black oil feed rate

Starting with black oil experiments, the productivity of the pilot plant reactor was investigated. Figure 4 demonstrates the effect of the raw material feed rate at constant oxygen flow rate on gaseous product composition. Both tests were carried out at nearly the same temperature in the reactor. Experimental data confirm the fact that an increase in oil feed rate shifts the reaction system to a more reduction regime. Higher selectivity to hydrogen and methane was observed in this case. On the other hand, the concentration of carbon oxides in the reaction product was lower. Thus, it is evident that the partial oxidation process is very sensitive to oxygen/carbon molar ratio (λ parameter). Very similar results can be expected in the case of white oil partial oxidation.

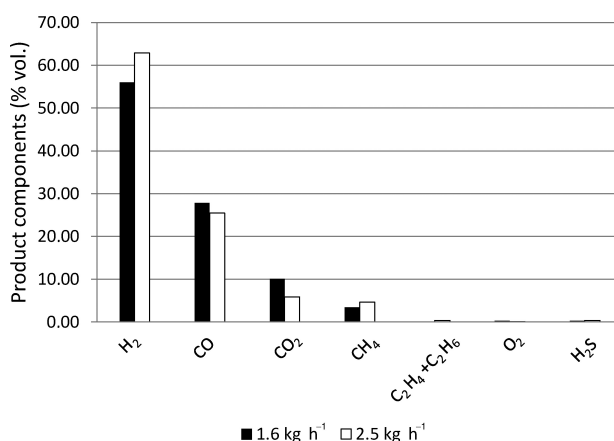


Fig. 4 – Effect of black oil feed rate on product composition, oxygen flow rate 1.3 kg h⁻¹, steam 1.5 kg h⁻¹; tests 5 and 7

Effect of oxygen flow rate

Lambda parameter is higher at the higher oxygen flow rate in the reactor at constant oil feed rate. Under such conditions, intensive formation of carbon oxides is supported. It is clear in this situation that the production of hydrogen and methane is suppressed, as can be seen in Figure 5, which demonstrates the results from white oil partial oxidation in tests 1 and 2 at the same feed rate and steam flow rate. A very similar result was obtained in the case of black oil partial oxidation in tests 3 and 6 – see Figure 6. Comparing all the results of black oil partial oxidation but at different process parameters (Figure 7) – tests 3 ~ 8, the trends of components concentration versus oxygen flow rate are the same.

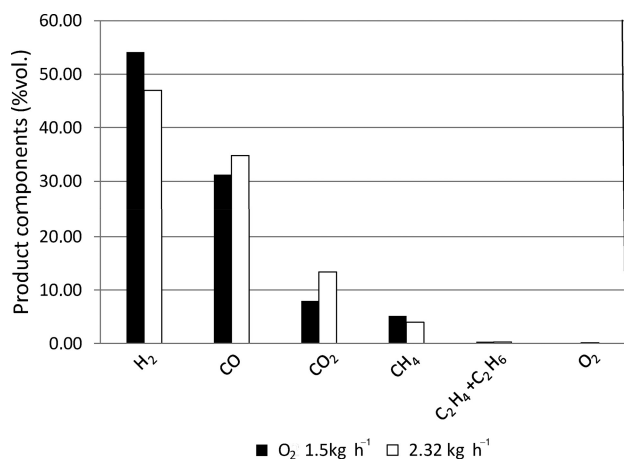


Fig. 5 – Effect of 54.6 % increase in oxygen flow rate on product composition, white oil partial oxidation, feed rate 1.5 kg h⁻¹, steam 1.0 kg h⁻¹; tests 1 and 2

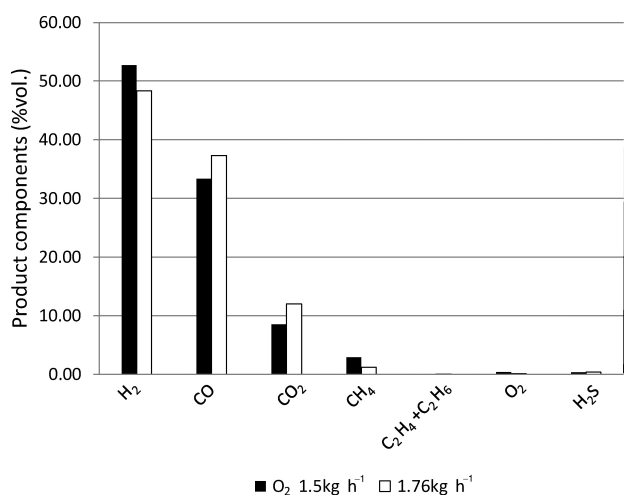


Fig. 6 – Effect of 17.3 % increase in oxygen flow rate on product composition, black oil partial oxidation, feed rate 1.58 kg h⁻¹, steam 1.0 kg h⁻¹; tests 3 and 6

Effect of nickel presence in the feed on black oil partial oxidation

Different crude oil fractions and hydrocarbon mixtures can contain small amounts of metals, mainly vanadium and nickel, which display catalytic properties in many reactions. This is why the effect of nickel content in the feed on POX process

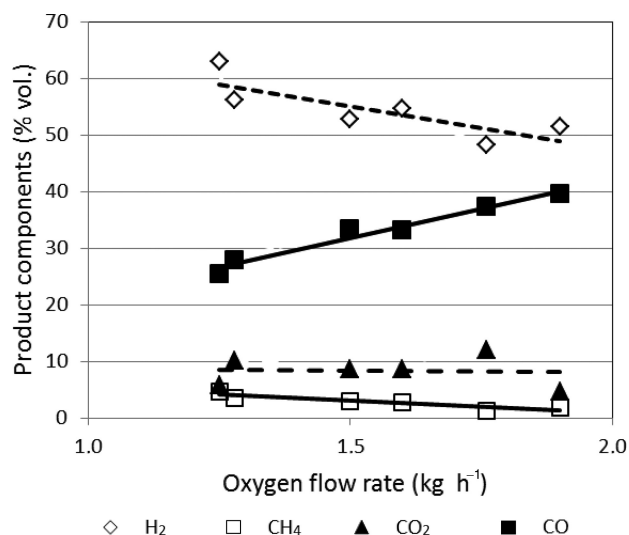


Fig. 7 – Effect of oxygen flow rate on black oil partial oxidation and product composition; tests 3 – 8

selectivity was investigated in this study as well. Characteristics of three raw materials containing a different amount of nickel, process conditions applied in experiments and concentration of main components in gaseous product are given in Table 3.

The selected results indicate neither the effect of raw material nor the “catalytic” effect of nickel concentration in the feed on the gaseous product composition. The reason for such reaction system behaviour lies probably in the very high reaction conversion rates of all components inside the „flame“, formed by the nozzle of the gasification reactor. In such a situation, the complex system of reactions reaches chemical equilibrium. This conclusion did not support our previous results³ which were observed in the case of gasification of a biomass/oil mixture in the presence of 1600 ppm nickel (in the form of 0.8 % wt. Ni(NO₃)₂ · 6H₂O) in the feed.

On the other hand, the presence of nickelacetylacetonate in the feed supported soot formation having 2 times higher specific surface and 3 times higher micropores volume in comparison to the experiment without nickel component in the white oil. The results are displayed in Figure 8. In addi-

Table 3 – Mass feed rates of hydrocarbon oils, oxygen and steam versus volume concentration of main gaseous components in partial oxidation product; temperature 1100–1140 °C

	Ni [ppm]	Feed [kg h ⁻¹]	O ₂ [kg h ⁻¹]	Steam [kg h ⁻¹]	H ₂ [% vol.]	CO [% vol.]	CO ₂ [% vol.]	CH ₄ [% vol.]
Mazut	31	1.58	1.5	1.0	52.68	33.35	8.54	2.00
Mogul HC-68	~ 0	1.50	1.5	1.0	54.09	31.23	8.00	5.17
Mogul HC-68 + Ni	364	1.60	1.5	1.0	54.27	31.44	8.22	5.05

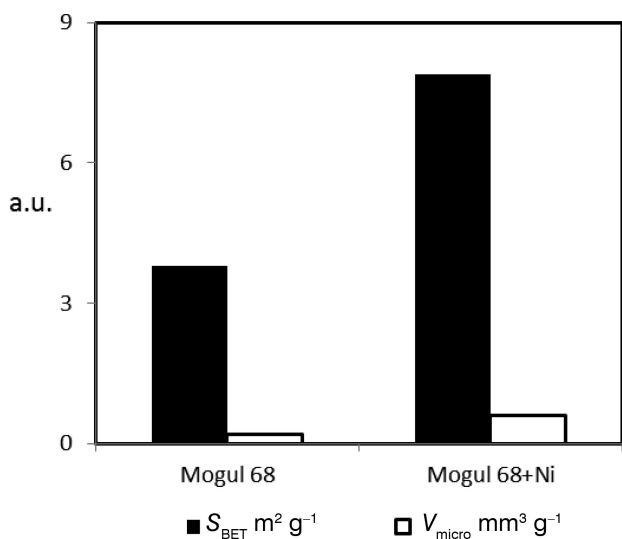


Fig. 8 – Effect of Ni on soot specific surface and micropores volume; experiments 2 and 9

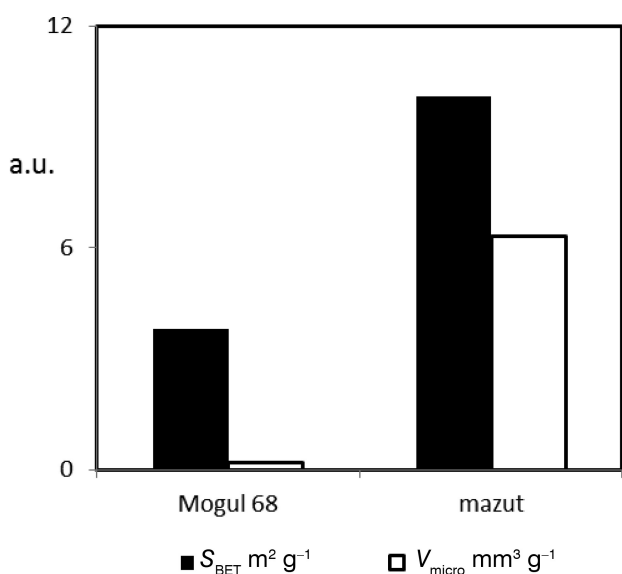


Fig. 9 – Comparison of soot parameters from white and black oil partial oxidation; experiments 2 and 3

tion, the presence of nickel organometallic complexes in mazut has an impact on soot porous structure as is evident from Figure 9 (see next section). Investigation of the soot formation mechanism should be recommended for the future research effort.

Effect of oil type on soot's parameters

First, the soot parameters – their specific surface and specific volume of micropores – formed during white and black oil partial oxidation were investigated. As can be observed from Figure 9, the type of process raw material has an influence on texture parameters of the soot. Application of mazut in partial oxidation resulted in soot formation of

both higher specific surface and specific volume of micropores in comparison to white oil Mogul 68. It could be said that the higher boiling point of oil of raw material is advantageous for production of perspective soot in applications for adsorption.

Soot properties versus process conditions

Feed rate of hydrocarbon at constant oxygen and steam flow rates has great influence on parameter lambda decrease. This operating condition manifests soot formation of higher specific surface (measured by BET method) as demonstrated in Figure 10. Higher specific volume of micropores was observed in this case as well.

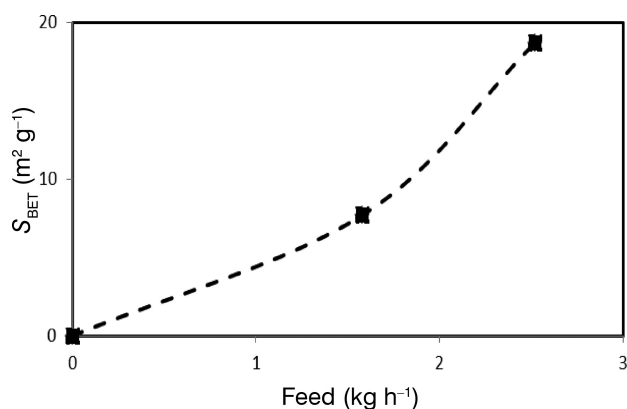


Fig. 10 – Effect of mazut feed rate on soot specific surface; experiments 5 and 7 ($\lambda = 0.81$ and 0.50 resp.)

Effect of elemental impurities on soot electrical conductivity

The main impurities in crude oil and thus in hydrocarbon wastes from crude oil fractionation and visbreaking process (VBR500) are typically represented as vanadium, nickel and iron. As evident from Figure 11, these elemental concentrations in the soot displayed great impact on the soot's electrical conductivity measured using polyethylene tapes filled with soot, (10 % w/w) from different POX tests. The contributions of nickel, iron and vanadium concentration in the soot on the tape's electrical conductivity were 40:20:7, respectively.

Relations between electrical conductivity and soot physicochemical properties

The presence of impurities in the reaction space during the partial oxidation process also significantly affects the physicochemical properties of the soot, which is formed as an important side-product. It is necessary to mention an idea about the forma-

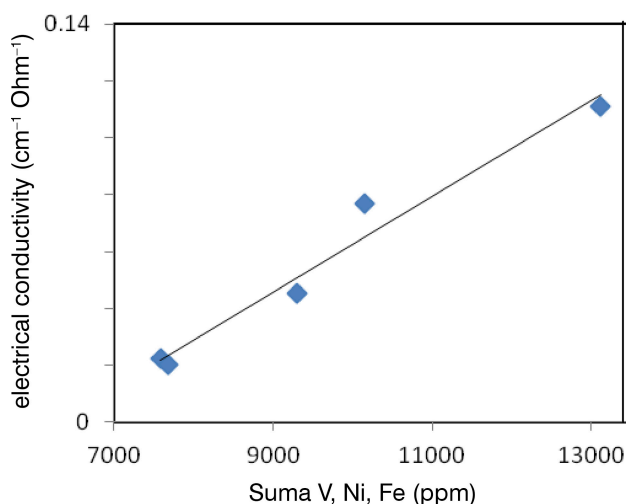


Fig. 11 – Effect of total concentration of main impurities on polymer electrical conductivity

tion of solid phase – the soot. The particles of soot have to rise in the reactor, by the desublimation process, from the hot gaseous reaction mixture which rate depends not only on solid particles growth rate but also on the nucleation process rate. The former process is responsible for final particles shape and size distributions. The latter process is probably affected by impurities presented in the feed whose catalytic effect on both the partial oxidation itself and the desublimation process can play a role as well.

A relation between electrical conductivity of polymer filled with soot and its physical properties is presented in the following Figures 12 and 13. It is expected that the higher nucleation rate in the case of the higher impurities content as nucleation centre have an effect the higher specific surface of the soot, see Figure 12. Consequently, the higher specific surface of the soot improves the adsorption

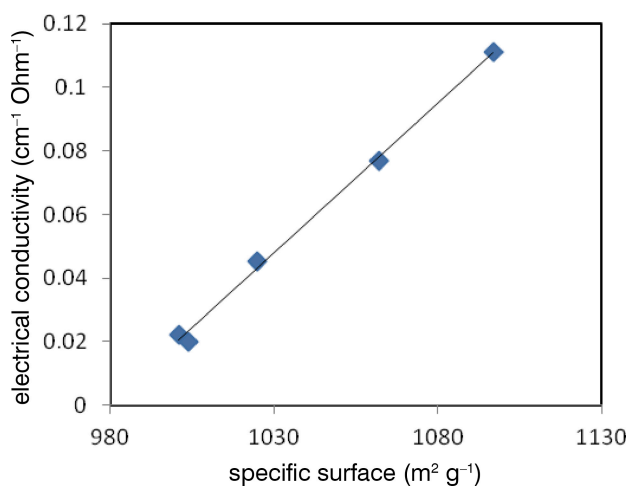


Fig. 12 – Polymer electrical conductivity versus soot specific surface

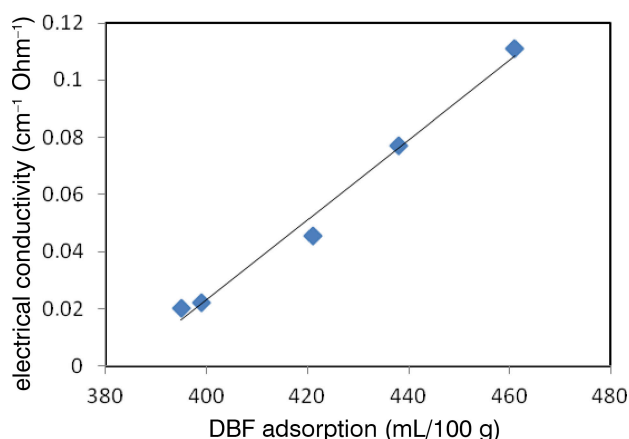


Fig. 13 – Polymer electrical conductivity versus soot adsorptivity

ability of the soot tested in the case of dibutylphthalate adsorption from contaminated water. The results are displayed in Figure 13.

Experimental data are useful for simple prediction of applicability of soot as filler for plastic materials based on key elements analysis (Ni, Fe, V) of POX raw material and/or specific surface or adsorption characteristics measurement of the soot. Sufficient electrical conductivity of polymers is a necessary condition for minimization of dangerous static electricity formation in the case of transportation of flammable liquids in plastic tubes or solid particles on transporters equipped with plastic components.

Conclusion

Based on pilot plant experiments, the paper describes basic parameters influence on selectivity of partial oxidation process. The gaseous product composition was very similar to Unipetrol RPA plant process parameters operating by Shell technology. During pilot plant tests, also soot was present in the raw gas. The soot amount was slightly higher because the pilot plant reactor operated at temperature below 1200 °C, see⁵. Investigation of the physico-chemical properties of the samples of soot formed during partial oxidation process were investigated as well. Its specific surface and micropore volume depend both on the type of hydrocarbon oil and its feed rate (lambda parameter). The presence of nickel in white oil supported the formation of higher both specific surface and micropore volume of the soot. Such material could be promising in adsorption process applications. At present, another effort is focused on numerical POX process model improvement.

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