Black and White Oils Partial Oxidation on Pilot Plant Unit

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BLACK AND WHITE OILS PARTIAL OXIDATION ON PILOT PLANT UNIT

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Introduction

An increased demand on hydrogen, which is essential for a deeper hydrorefining 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[1-3]. Process POX is based on reaction between raw material and oxygen in the presence of water vapour[4-6] and its selectivity with regard both to composition of the exhaust gas and soot formation 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 reaction in the reaction space.

The raw material is gasificated in industrial plants[4] typically at temperature above 1300 °C under pressure 3.5 MPa. The performance of the operating unit enables to produce (in the reaction space of 1 m^3) 1500 m^3/h of synthesis gas of a typical composition (% vol.):

H_2 = 49.3; O_2 = 6.8; CO = 46.0; CH_4 = 0.2; (N_2 + Ar) = 1.1; H_2S = 0.7

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 the UNIPETROL RPA Co., which operates according to the license of the Shell Co[4]. Significant formation of carbon black – soot - as a by-product of partial oxidation under the process conditions has to be separated. Its production can be monitored by discharge of soot dispersion in water, which arises at product quench cooling by water after outlet from the POX reactor. An impact 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.

Experimental

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 (masut), white oil (base oil Mogul HC 68) and white oil with nickel (*II*) acetylacetonate (0.16 % wt.). All these materials were analyzed for kinematic viscosity (1348 and 56 mm^2/s at 40 °C, resp.), density (963 and 869 kg/m^3 at 20 °C, resp.) and elemental composition, see Table I. Special attention was paid also to a catalytic effect of nickel concentration in the base oil Mogul HC68 POX on product composition.

Table I
Elemental composition of raw materials

[% wt.]	C	H	S	N	Ni	Fe	Total
Masut	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

Pilot plant unit

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 with auxiliary electrical heating system, 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 free 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.

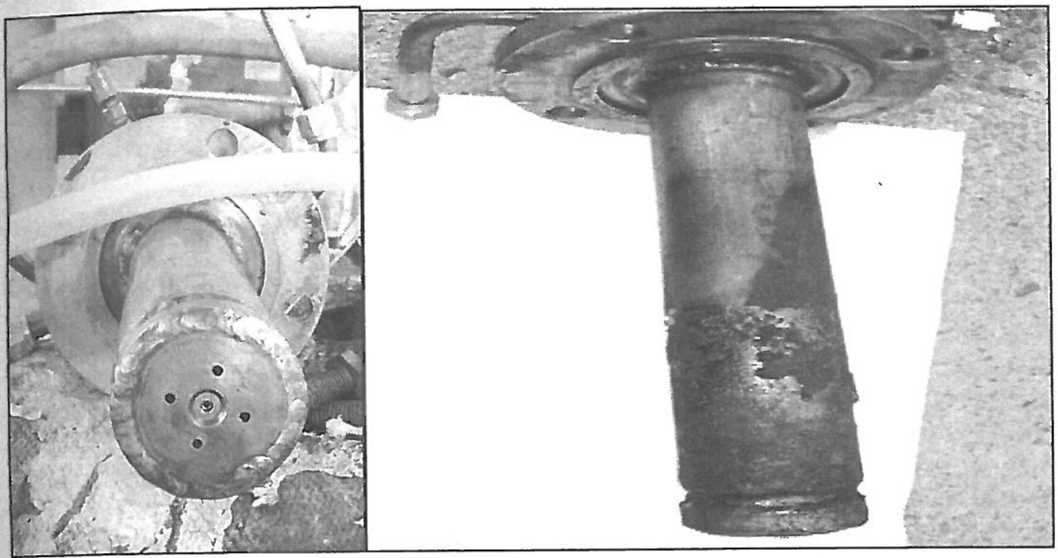

Figure 1. Co-annular nozzle of pilot plant reactor before (left) and after (right) experimental test

Reaction product was quenched, cooled down and washed by water. The produced gas mixture was regularly sampled and analysed by GC method and subsequently was introduced into a furnace due to the disposal of flammable hydrogen and carbon monoxide from the unit. Digital parameters measurement and apparatus control were made by data acquisition system using WinControl 2005 software. Based on GC analysis reactor steady state achieving was monitored. After reaching the pilot plant unit steady state subsequent three independent samples were taken in order to increase accuracy of measurement. The data were used for determination of mean reaction product composition. Also, 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 specific surface area (measured by N_2 adsorption) is typically above 800 $m^2 g^{-1}$.

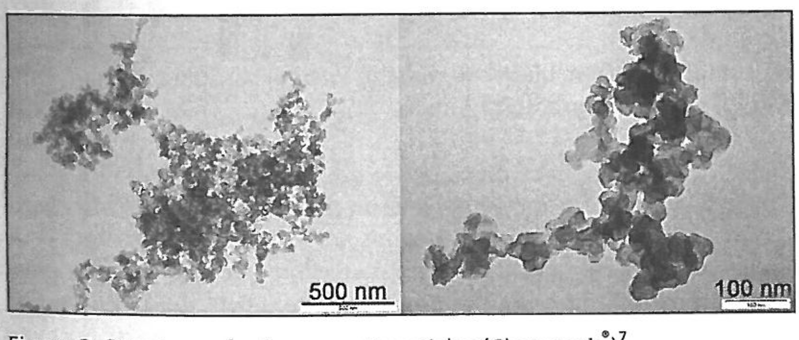

Figure 2. Structure of primary soot particles (Chezacarb®)[7]

Results and discussion

Raw materials their feed rates, oxygen and steam flow rates during experimental partial oxidation tests on pilot plant unit are summarized in Table II. Typical mean temperature in reactor was controlled within interval 1150-1200 °C and nearly ambient pressure was applied (0.11 MPa).

Table II
Parameters of experimental tests

Test	Raw material	Feed [kg/h]	O_2 [kg/h]	Steam [kg/h]
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 - Masut	1.58	1.50	1.00
4	Black oil - Masut	1.98	1.90	0.62
5	Black oil - Masut	1.58	1.28	1.51
6	Black oil - Masut	1.57	1.76	1.00
7	Black oil - Masut	2.52	1.25	1.52
8	Black oil - Masut	1.98	1.60	1.22
9	Mogul HC 68 + Ni	1.57	1.50	1.00

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 partial oxidation process. Black oil (masut), white oil (base white oil Mogul HC 68) differs mainly in boiling point, viscosity and also in content of impurities (e.g. nickel). Figure 3 presents effect of raw material on gaseous product composition, i.e. main components – hydrogen, carbon oxides, methane, ethane&ethylene, sulfane and also non-reacted oxygen (water vapour was not detected). It is evident that contents of components are very close each other in case of compared tests 2 and 3.

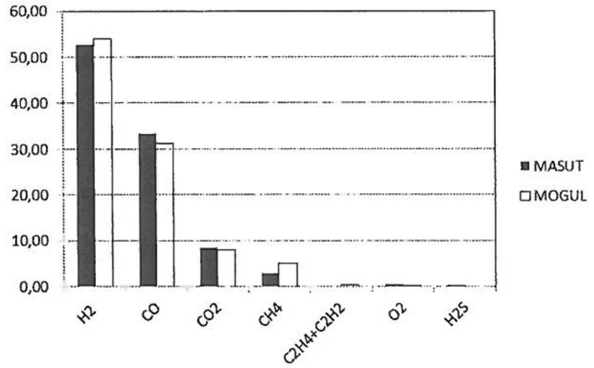

Figure 3. Comparison of gaseous product composition from black and white oils partial oxidation.
Feed rate 1.58 and 1.5 kg/h, oxygen 1.5 kg/h, steam 1.0 kg/h; tests 2 and 3

Effect of black oil feed rate

Starting with black oil experiments a productivity of pilot plant reactor was investigated. Figure 4 demonstrate effect of feed rate of raw material at constant oxygen flow rate on gaseous product composition. Both tests were made at nearly the same temperature in the reactor. Experimental data confirm the fact that increase of oil feed rate shift the reaction system to more reduction regime. The higher selectivity to hydrogen and methane was observed in this case. On the contrary concentration of carbon oxides in the reaction product was lower one. Thus it is evident that that the partial oxidation process is very sensitive to oxygen / carbon molar ratio (lambda parameter).

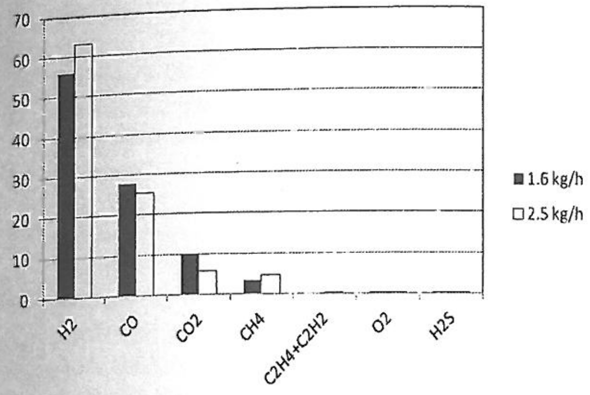

Figure 4. Effect of black oil feed rate on product composition
Oxygen flow rate 1.3 kg/h, steam 1.5 kg/h; tests 5 and 7

Effect of oxygen flow rate

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

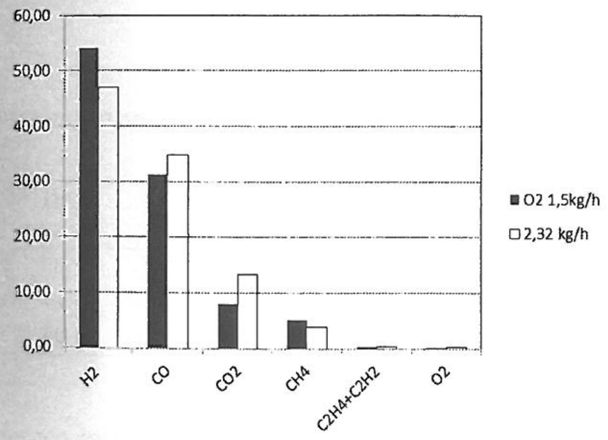

Figure 5. Effect of 54.6 % increase of oxygen flow rate on product composition
White oil partial oxidation, feed rate 1.5 kg/h, steam 1.0 kg/h; tests 1 and 2

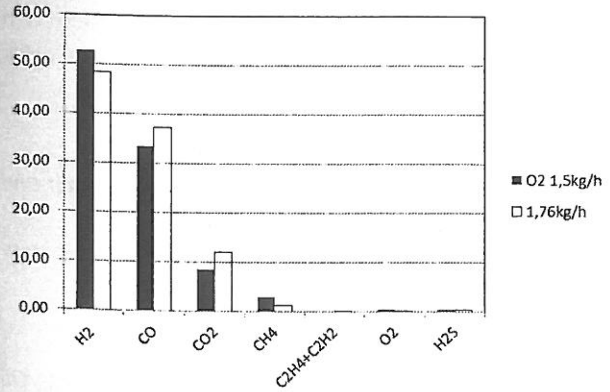

Figure 6. Effect of 17.3 % increase of oxygen flow rate on product composition
Black oil partial oxidation, feed rate 1.58 kg/h, steam 1.0 kg/h; tests 3 and 6

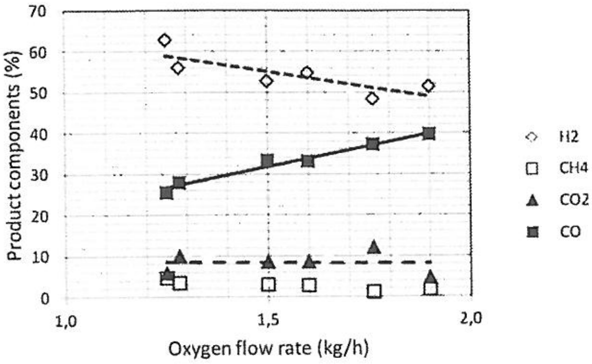

Figure 7. Effect oxygen flow rate on black oil partial oxidation on product composition, tests 3 – 8

Effect of nickel in the feed on black oil partial oxidation

Different crude oil fractions and hydrocarbon mixtures can contain small amount of metals, mainly vanadium and nickel which display catalytic properties in many reactions. That is why the effect of nickel content in the feed on POX process selectivity was investigated in this study as well. Characteristics of 3 raw materials containing different amount of nickel, process conditions applied in experiments and concentration of main components in gaseous product are given in the Table III.

The selected results indicate neither effect of raw material nor "catalytic" effect of nickel concentration in the feed on the gaseous product composition. The reason of reaction system behaviour consists probably in very high reaction conversion rates of all components just inside „flame", formed by nozzle of the gasification reactor. In such situation the complex system of reactions reach the chemical equilibrium there. This conclusion did not support our previous results[3] which were observed in case of gasification of the biomass / oil mixture in the presence of 1600 ppm nickel (in the form of 0.8 % wt. $Ni(NO_3)_2.6H_2O$) in the feed.

Table III

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]	O_2 [kg/h]	Steam [kg/h]	H_2 [% vol.]	CO [% vol.]	CO_2 [% vol.]	CH_4 [% vol.]
Masut	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

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, see[4]. Investigation of physicochemical properties samples of soot is under way now and results will be presented in another our paper. At present another effort is focused to numerical POX process model formulation. Comparison of experimental data and simulation results will be reported later.

Acknowledgements

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