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Paper brings main results of research project *"Investigation of hydrogen and synthesis gas production by gasification of waste biomass from biofuels production"*, supported by Ministry of Industry and Trade of the CR. Also fresh results reached in frame of a subsequent applied research project "*Pilot plant unit support for POX Process – identification of external feedstock*" are discussed as well. Catalytic effect of iron nanoparticles or nickel nitrate as catalysts in improvement of the pilot plant biomass/oil partial oxidation was confirmed in the study.

Keywords: *hydrocarbon oil, biomass, catalytic partial oxidation, nickel, iron nanoparticles*

Introduction

One of potentially useful process of hydrogen production from fossil and renewable natural sources via synthetic gas seems to be partial oxidation (POX) and gasification of biomass material like meal rape from rape oil and/or bio-diesel production [1-3]. A motivation for research and development sector is based on intention to intensify hydrogen production. There is an opportunity for utilization of biomass waste like rape meal resulted from fuels bio-components production.

Common partial oxidation of hydrocarbon visbreaking vacuum flashed cracked residue and meal rape which is bio-waste from fuels bio- components production was investigated in our previous study [3]. The important difference between both feed materials is as follows: Meal rape contains only one half of carbon, but much more oxygen, water, and inorganic components (forming ash after its burning) of that level corresponding to hydrocarbon oil. Also, the higher oxygen content of meal rape suppresses its specific combustion heat value. Main products of POX carbon monoxide, carbon dioxide and hydrogen are accompanied by sulphur and nitrogen compounds which are necessary to remove or transform by interrelated process units.

The partial oxidation is typically described by various chemical reactions, the resulting products of which depend not only on the raw material composition but also on the reaction conditions. The threshold composition of reaction products is given by chemical equilibrium. Concentrations of oxygen, methane, carbon dioxide and carbon monoxide and hydrogen in reaction product can be used to calculate the apparent equilibrium temperature.

Ideal combustion produces only carbon dioxide and water. The partial oxidation process can be characterised by parameter lambda which is a measure of reduction conditions for assessment of hydrocarbon gasification. Parameter lambda is a ratio of oxygen amount actually supplied to the gasification process with respect to the mass of oxygen which is necessary for ideal combustion. It is evident, that oxidation regime is typical by lambda value greater than 1. In this case carbon dioxide and water are formed predominantly. On the otherhand, hydrogen and carbon monoxide are formed under reduction conditions characterized by lambda value less than 1.

Experimental

Pilot POX reactor of I.D. 0.3 m and overall length 2 m was furnished by of electrical heating to control pseudo adiabatic regime at temperature interval 1000-1200 °C. The inner reactor wall was equipped by the thermal insulation layer. Temperature profile was monitored in 3 equidistant points along the reactor by thermo-elements. Pilot plant unit for partial oxidation was equipped by water steam generator, continuous suspension batcher, gasification reactor equipped with co-annular feeding jet burner, water quench and heat exchanger.

Suspension of dry biomass alone or with catalyst (iron nanoparticles or nickel nitrate) in mineral oil (feed rate 1.5–3.0 kg/h) was fed to the reactor via internal co-annular jet and partially combusted in oxygen - water steam atmosphere (oxygen flow rate 2–3 kg/h and steam feed rate 1.25 kg/h) to produce carbon monoxide and hydrogen as main gaseous components in the reaction product with small amount of carbon dioxide and methane. GC analysis was applied for monitoring of gaseous product composition.

The basic experiment consisted in gasification of pure mineral oil (carbon and hydrogen content 87 and 13 %wt., respectively). This was a matrix, in which we added other elements, such as biomass and/or a catalyst. Typical gasification conditions were as follows: Mass ratio of fuel and water steam: 1.65; mass ratio of fuel and oxygen: 0.49; temperature profile within the reactor: 1150- 1180°C; Lambda: 0.62; Mean residence time of reaction mixture within the reactor: 17.5 s.

Results and Discussion

Process Simulation

Complex chemical composition of the feed was solved by concept of representative chemical compounds resulting in the same elemental composition as the original raw material mixture. Instead of detailed waste rape meal composition, e.g., consisting of cellulose, lignin, proteins and phospholipids, similar compounds (glucose, vanillin, n-butyl-stearate, methionine and tri-ethyl-phosphate) were applied for process simulation. Physicochemical data of these compounds are available in the Aspen Plus software database [4] and were applied for isothermal chemical equilibrium reactor model combined with water quench of flue gas. Model of apparatus incorporate heat exchangers and phase separator as well. Chemical and phase equilibrium was calculated by Gibbs function minimization method.

Hydrogen production in syngas mixture depends both on oxygen and water steam ratio to fed biomass and hydrocarbon oil mixture, reaction temperature and flow characteristics of the reactor. Typical simulation result of partial oxidation for meal rape to hydrocarbon oil 1:10 (wt.) feed ratio was as follows: adiabatic temperature of product = 1038 °C; molar ratio of CO / CO_2 in product = 8.08; hydrogen and carbon monoxide molar fraction = 0.487 and 0.358, respectively.

Pilot plant experiments

Experimental tests with feed composition changed from pure high boiling hydrocarbon oil to 5 % wt. and 10 % wt. biomass in oil produced following hydrogen and carbon monoxide content in product stream (Rest CO_2 and ~ 1 % CH_4): 33.4, 35.5, 33.9 % vol. of H_2 and 30.4, 31.8, 31.6 % vol. of CO, respectively.

Simplified model of one CSTR with the same reaction time of all reaction steps was used for simulation of equilibrium reactions. Qualitative agreement of experimental results with process simulation can be seen in Figure 1.

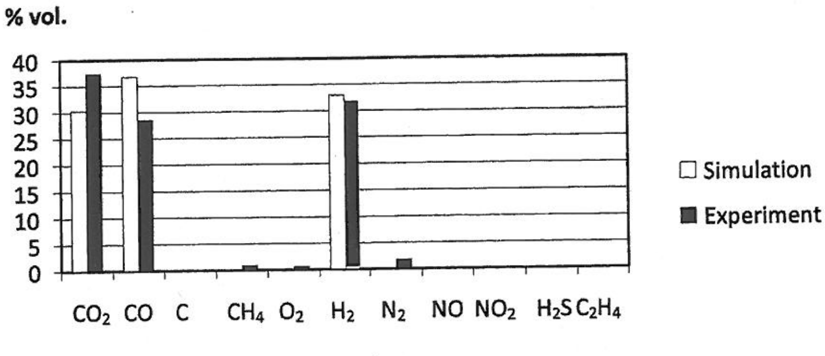

Fig. 1: Partial oxidation of 5% meal rape in oil – simulation versus experiment oxygen : steam (2.5 : 1.25 kg/h); feed rate 2 kg/h; temperature 1210 °C.

Model and experimental results agreement is good from the chemical engineering data point of view. Similar content of carbon oxides and nearly the same hydrogen concentration verifies simulation mass balance. The higher value of carbon dioxide concentration in the product implies the fact that presumptions of both ideal mixing in reactor and/or complete chemical equilibrium are not totally fulfilled in case of pilot plant unit.

Partial oxidation regime strongly influenced the product composition. The effect of lambda parameter on components concentration in the product has been described in our previous study [3]. An experimental effort resulted in observation that optimum lambda value lies in interval 0.6 – 0.8 . In case of more intensive reduction regime the dominant production of methane was found. On the other hand, increasing the lambda parameter value (above 1) the hydrogen production decreased to zero value.

Catalytic partial oxidation

Experiment with pure hydrocarbon oil was compared with a test in which 0.4 wt. % of nanoscale iron particles were added to mineral oil. For next test, nickel addition to the fed oil (in the form of nickel nitrate 0.8 % hm. $Ni(NO_3)_2.6H_2O$) was applied. Product compositions are compared in Table I. It is evident that the presence of iron has no impact on the content of hydrogen in the product. Only the content of CO in outlet gas was slightly higher on the contrary of CO_2 and methane concentration.

Replacement of iron by an addition of 0.8 % hm. $Ni(NO_3)_2.6H_2O$ in the subsequent experiment called for much higher hydrogen and lower CO_2 concentration in the product. There is clear evidence about higher catalyst effects of nickel than iron particles. It is surprising that in all experiments the outlet gas contains also traces of methane, although there should be none at the theoretical equilibrium composition. The process was probably far from chemical equilibrium conditions and kinetics controlled the reaction conversion.

Partial oxidation of suspension of mineral oil and 5% meal rape (solid biomass rest after pressing of oil) was studied also in presence of catalyst particles in a form of nano-iron which was added to the feed in concentration 0.4 %wt. Temperature in the reactor was in this case in interval 1100-1180 °C and feed rate to steam and oxygen ratios were set to 1.6 and 0.46 , respectively. Corresponding lambda value was equal to 0.61 . Experimental product composition in case of catalytic and non-catalytic partial oxidation is compared in Table II with theoretical reaction mixture composition corresponding to chemical equilibrium. These results indicate positive effect of nano-iron particles in reactor. It is seen that catalyst accelerates the pyrolysis process and thus concentrations of main product components are in this case closer to chemical equilibrium.

Table I: Catalytic effect of nano Fe particles or Ni (%wt. in the feed) on gaseous products during mineral oil partial oxidation

	none catalyst	**0.4 % Fe**	**0.16 % Ni**
H_2	36.1	36.5	45.73
CO	29.4	32.9	29.68
CO_2	32.8	29.8	23.23
CH_4	1.7	0.8	1.36

Table II: Product composition for non-catalytic and catalytic POX of 5% meal rape in mineral oil compared to chemical equilibrium values (% vol.)

	POX	**CPOX**	**Equilibrium**
H_2	34,3	41,6	48,9
CO	36,3	33,9	41,5
CO_2	22,6	19,7	9,53
CH_4	5,8	4,3	0

Conclusion

This paper brings pilot plant results about possibility of common partial oxidation of hydrocarbon and rape meal and evidence about positive catalytic effect of mainly nickel and in less extent iron nanoparticles on reaction conversion. It was observed that the presence of Ni and Fe catalyst in the feed has a positive impact on hydrogen output and supports formation of carbon monoxide and suppress content of methane in the gas product. Experimental data were well compared with process simulation based on equilibrium reactor model. Oil can be saved if a part of it is replaced by biomass. Therefore this modified technology can be applied to recover prospective commodities from renewable sources.

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