Evaluation of Liquid Hydrocarbons Formation and Energy Consumption in Consecutive Biomass and Carbon Feedstock to Liquid Hydrocarbons Transformation Process

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Abstract: Evaluation of liquid hydrocarbons formation and energy consumption during biomass and carbon containing feedstock was provided. For experiments birch, spruce saw dust, bottom peat, peat moss and brown coal were used. Experiments were provided using semi-laboratory set-up consists of gasification furnace for water gas shift reaction, methanol synthesis reactor and hydrocarbons synthesis reactor. The highest liquid hydrocarbons yield was found to be 0.72 kg(Hydrocarbons)/kg(initial source) for brown coal. The lowest liquid hydrocarbons yield 0.51-0.55 kg(Hydrocarbons)/kg(initial source) was found for wood residuals. Deferent types of peat characterizes by medium liquid hydrocarbons yield 0.62-0.64 kg(Hydrocarbons)/kg(initial source). For all substrates a negative heat balance was obtained. The highest values of energy needed to be inputted in the system were found to be 4.8 MJ/kg for brown coal. The lowest value of energy needed to be inputted in the system was found to be 3.3-3.6 MJ/kg for wood residuals. In all cases liquid hydrocarbons consists of 1-7 wt. % paraffins, 1-2 wt. % olefins and 90-95 wt. % of various aromatic compounds.

Key-Words: - Syn-gas, biomass gasification, methanol synthesis, methanol to hydrocarbons transformation process, wood, peat, brown coal, law valuable carbon sources

1 Introduction

Modern chemical technology of synthetic hydrocarbons production is based on two methods for hydrocarbons synthesis: Fischer-Tropsch synthesis [1, 2], and the formation of hydrocarbons through methanol synthesis [3], followed by its transformation into hydrocarbons. Both methods for producing hydrocarbons use hydrogen-enriched synthesis gas as starting compounds, while the H_2/CO ratio should be in the range of 2.1–3.3. Gasification of carbon-containing raw materials [4] can be considered as basis for syn-gas producing suitable for further utilization in to liquid hydrocarbons. Industrial use of solid carbon-containing raw materials for the production of synthesis gas is negligible due to technical problems and insufficient study of the process [5]. However, the reserves of solid carbon-containing fuels, including fully or partially renewable, are several times higher compare to natural gas or raw oil. Therefor it possible to consider solid fuels and solid carbon containing wastes as the main feedstock for the chemical industry, power generation and automobile transport in the nearest future due to decrease natural gas and raw oil resources. Thus, all of these necessities lead to provide a comprehensive study of the liquid hydrocarbons production using solid fuels.

Steam gasification of solid fuels is possible in various ways including: gasification in a stationary or moving and fluidized bed. Each of the above methods is characterized by its advantages and disadvantages. Carrying out gasification in a moving bed of feedstock with a downward flow of gas is most promising for producing gas enriched with hydrogen [5]. During the gasification of solid fuels a large number of chemical transformations occur. In gasification plants of this type, several main reaction zones are distinguished, distributed over the height of the reaction tube. In the upper section of the gasifier, the materials are dried at a temperature of 120-250°C. Subsequently, the gasification material enters the zone with a temperature of 250-800 ° C, where its partial pyrolysis takes place. Air/oxygen and steam are supplied to the central part of the gasifier, while solid materials are oxidized, accompanied by high heat generation, the temperature of this zone is 800-1100 °C. In the lower part of the reactor, the resulting gases are reduced at a high temperature, a temperature of 800-1100 °C.

At the same time, regardless of the method used, the obtained syn-gas contains a large amount of impurities and requires purification from carbon dioxide, nitrogen oxides, hydrogen cyanide, hydrogen sulfide and carbon monoxide sulfide [1-5]. Currently, for this purpose, the most commonly used two-stage purification of synthesis gas includes a stage of absorption cleaning with alkaline solutions from carbon dioxide, nitrogen oxides and hydrogen cyanide and a stage of chemisorption cleaning from sulfur-containing compounds. The synthesis gas should not include more than 0.006 mol/m^3 of sulfur-containing compounds. The active phase of the last stage of syn-gas purification contains zinc, magnesium, nickel, copper, manganese, molybdenum, iron, tin oxides. Several reaction processes takes place on the surface of such systems including the hydrolysis of COS compounds, the interaction of hydrogen sulfide and sulfur dioxide with the metal oxide phase of the sorbent. The main characteristics of the effective operation of such systems is the maximum chemisorption capacity.

On the next step cleaned syn-gas can be converted in to methanol [3] by catalytic transformation. Currently, there are gas-phase (two-phase) and liquid-phase (three-phase) catalytic methanol synthesis methods. When developing highly efficient gas-phase synthesis units, it is necessary to overcome a number of difficulties related to the non-uniform distribution of the gas flow and temperature over the cross section and height of the reactor. A significant part of these problems can be solved using a liquid-phase synthesis in the system “gas-catalyst-inert solvent” on catalyst slurry. The advantages of this approach include: the simplicity of the reactor design, a fairly uniform distribution of liquid and gas over the cross sectional area of reactor, the possibility of introducing and removing the catalyst from the system without stopping it, a relatively low axial diffusion of gas and efficient use of reaction heat. Abrasion and catalyst losses are significantly lower than in gas-phase "boiling" systems due to the elastic properties of the liquid medium. It should also be noted that with liquid-phase methanol synthesis, a more favorable equilibrium state of the system can be ensured, which makes it possible to significantly increase the equilibrium concentration of methanol in the reaction mixture as compared with gas-phase synthesis. The degree of conversion of carbon oxides to methanol for the "liquid phase" process depends on the relative amounts of the liquid and gas phases. With an increase in the relative proportion of the solvent or when it is replaced with a solvent having a large absorption capacity with respect to methanol, the equilibrium degree of conversion of carbon oxides also increases.

The final step of hydrocarbons formation is methanol to hydrocarbons transformation process [3]. The basis of the methanol pathway for producing hydrocarbons is the conversion of methanol to dimethyl ether and the transformation of a mixture of methanol and dimethyl ether into olefins, paraffin and aromatic hydrocarbons. Olefins, in turn, are also transformed into aromatic and aliphatic hydrocarbons. As a result of the synthesis, an equilibrium mixture of olefins, aromatic hydrocarbons, water and ballast gases (CO, CO_2, CH_4) is formed. The conversion of methanol to hydrocarbons on aluminosilicate catalysts is more promising than the Fischer-Tropsch process due to the high yield of hydrocarbons. However, the stability of currently used catalytic systems is insufficient, which requires the development of new catalysts and modification of industrially existing catalytic systems.

Here an application of semi laboratory set up for combined power and fuel compounds generation by consecutive biomass to liquid hydrocarbons processing is discussed.

2 Reaction set up description and experiment methodology

Experiments were provided using set-up shown on Figure 1. A biomass feedstock enters receiver bunker (1) and dose in to gasification furnace (2) where it mixes with water steam to provide hydrogen and carbon monoxide formation. Wet syn-gas flows through reflux (4) where water steam condenses and flows in to water collector (3). Quantity of syn-gas is measured by gas meter (5). Syn-gas is cleaned from sulfur containing substances in wet scrubber (6) using trimethylamine for acid gases capture and absorber (7) using zinc oxide for desulfurization. Than cleaned syn-gas is compressed by compressor 8 up to 15 Bars and enters methanol synthesis reactor (9) field with mixed copper and zinc oxide catalysts. A syn-gas is separated from methanol in reflux (10) and enters condenser (11). Formed methanol flows in to two stage methanol to hydrocarbons synthesis reactor (12). Dimethyl ether is formed on the first stage using alumina as a catalyst. Dimethyl ether separates from water in reflux (13) and water separator (14) and enters dimethyl ether to hydrocarbons transformation section of the reactor. Liquid hydrocarbons separate from dimethyl ether in reflux (15) and hydrocarbons separator (16). Gas hydrocarbons and unreacted dimethyl ether return into reactor using compressor (17).

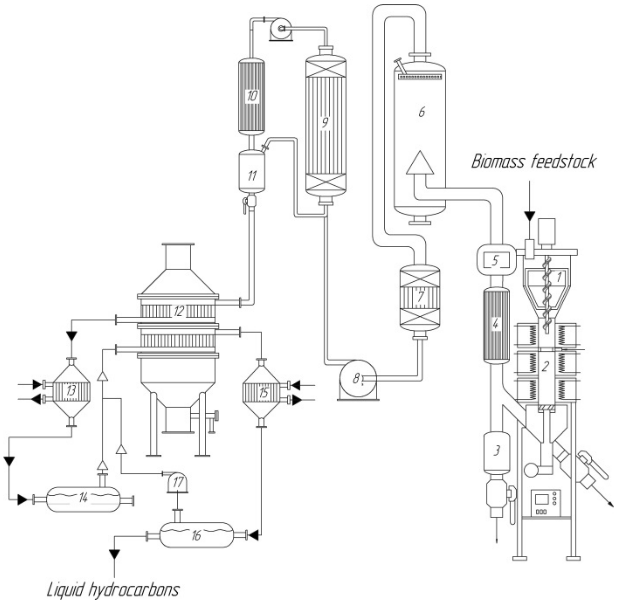

Fig.1 Reaction set up for carbon containing feedstock conversion in to liquid hydrocarbons. (1 – receiver bunker for biomass feedstock, 2 – gasification furnace, 3 – condensed water collector, 4 – heat exchanger, 5 – gas meter, 6 – wet scrubber, 7 – sulfur substances adsorber, 8 – syn-gas compressor, 9 – liquid phase syn-gas in to methanol transformation reactor, 10 – methanol condenser, 11 - methanol separator, 12 – two stage methanol to liquid hydrocarbons transformation reactor, 13 – water from dimethyl ether condenser, 14 – water from dimethyl ether separator, 15 – liquid hydrocarbons condenser, 16 – liquid hydrocarbons from dimethyl ether separator, 17 – dimethyl ether and gas phase hydrocarbons compressor).

In typical experiment 1 kg/h of biomass feedstock was loaded in to gasification furnace. Gasification furnace temperature was maintained at 800^0C in gasification zone. Water steam flow rate was maintained 1.4 kg/h, steam initial temperature 200^0C. Methanol synthesis reactor was field with 10 kg MEGAMAX® 500 Zn/Cu catalysts (Clariant AG, Germany), reaction zone temperature was 240^0C and reaction pressure was 20 Bar. Methanol to hydrocarbons transformation reactor was field with two types of catalyst. The first zone of reactor was field with 5 kg of γ-alumina (Reachem, Russia) for methanol to dimethyl ether transformation and the second zone was field with 5 kg H-ZSM-5 (HKC, Hong Kong, China). The reaction zone temperature was 350^0C.

For the analysis of the liquid organic phase, a gas chromatograph (Kristallux 4000M, Russia) equipped with a flame ionization detector was used. Samples were analysed using a ZB-1 capillary column, l = 30m, d = 0.32 mm, T_{max} = 310 °C. The temperature of the sample evaporator is 300 °C, the temperature of the flame ionization detector and the thermal conductivity detector is 250 °C. The column temperature was maintained at 40 °C for the first five minutes after the sample was introduced into the column, after which temperature rise up to 275 °C at a rate of 10 °C/min and was maintained throughout the analysis. The carrier gas flow rate was maintained at 20 ml/min, the hydrogen flow rate was 25 ml/min, and the air flow rate was 250 ml / min. The duration of the analysis was 1 hour. The qualitative determination of the components was carried out using a mass spectrogram obtained by the previous method, as well as using standards. Quantitative determination of the organic substances concentration was made according to ASTM D 5134-2003. Quantity of organic hydrocarbons substances was measured gravimetrically. Heat consumption or output was performed using heat meter LRF-3000SW-R maintained in heat exchanger units of furnace, methanol synthesis reactor, methanol to hydrocarbons synthesis reactor.

3 Results and discussions

For experiments birch, spruce saw dust, bottom peat, peat moss and brown coal were used. The elemental compositions of the source materials are presented in Table 1. The composition of peat corresponds to the elemental composition of medium ash peat moss. The composition of bottom peat, coal and wood also corresponds to the interval values of the elemental composition for the respective materials. The increase of sulfur concentrations in the samples is noticeable during transition from wood to brown coal.

Table 1. Elemental composition of source materials

Wt.* %	Birch	Spruce	Peat moss	Bottom peat	Brown coal
C	48.19	51.9	53.3	57.6	68.3
H	6.2	5.7	5.7	3.8	2.4
N	0.7	0.4	0.6	0.4	0.01
S	0.01	0.03	0.1	0.3	0.7
O	43.3	39.39	34.6	30.7	20.19

* - elemental analysis was provided according to ASTM D3176 – 15

The study of the elemental composition of ash for the above samples of raw materials showed the presence of Ca, Mg, Fe, Al, K, Na in the composition of the samples (Table 2), with prevalence of Ca.

Table 2. Elemental composition of ash

Wt.* %	Birch	Spruce	Peat moss	Bottom peat	Brown coal
Ca	25.1	21.3	48.4	56.2	42.7
Mg	1.4	0.6	11.4	12.4	14.3
Fe	0.9	0.4	15.7	14.3	21.3
Al	0.1	0.2	1.7	1.2	2.1
K	0.7	0.9	4.6	3.1	2.4
Na	0.4	0.9	2.9	1.4	1.7

* - elemental analysis was provided according to ASTM D3176 – 15

At the same time, a higher Ca content is observed in the composition of bottom peat. It is necessary to note a significantly higher content of magnesium and iron for peat. Brown coal is characterized by the presence of a highest amount of iron that can be explained by chemical characteristics of the geological deposits. Elemental analysis of the resulting ash showed the absence of heavy metals in compositions of all source materials. A synthesis gas of different composition was obtained (Table 3) after gasification furnace.

Table 3. Syn-gas production specific volumes and gas composition obtained for different source materials

Vol.* %	Birch	Spruce	Peat moss	Bottom peat	Brown coal
CO	12.4	11.2	14.3	13.1	12.8
CO_2	34.6	34.3	33.5	32.6	29.7
H_2	35.6	36.8	33.7	35.9	37.3
N_2	9.6	9.4	10.1	9.4	9.8
CH_4	6.6	6.7	6.9	6.3	6.8
C_2H_2	0.01	0.01	0.01	0.04	0.02
C_2H_4	0.87	0.95	0.99	0.57	0.43
C_2H_6	0.11	0.15	0.1	0.2	0.5
SO_2	0.01	0.01	0.03	0.07	0.11
NO	0.01	0.01	0.02	0.03	0.04
$V_{syn\text{-}gas}$, m^3_n/kg	4.28	4.34	4.47	4.42	4.51

* - gas analysis was provided according to ASTM D1945 – 14

The H_2/CO ratio varies from 2.4 to 3.3 in syn-gas, however this values are suitable for methanol synthesis process, after additional purification. The presence of ballast gases is typical for all samples: about 10 vol. % nitrogen, 33-37 vol. % CO_2, 7-8% flammable gases. Total gas yield was 1.2-1.5 m^3 n.c. per 1 kg of dry raw materials. Sulfur oxide and nitrogen oxide presents in all samples of syn-gas. The concentration of sulfur dioxide and nitrogen dioxide is higher for peat and brown coal compare to different types of wood. The presence of sulfur dioxide and nitrogen dioxide impurities in the composition of the resulting synthesis gas makes it necessary to further purification before further use.
The gas composition after purification presents in table 4.

Table 4. Syn-gas composition obtained for different source materials after adsorber

Vol.* %	Birch	Spruce	Peat moss	Bottom peat	Brown coal
CO	19.02	17.18	21.93	20.09	19.63
CO_2	0.02	0.03	0.02	0.03	0.02
H_2	54.60	56.44	51.69	55.06	57.21
N_2	14.72	14.42	15.49	14.42	15.03
CH_4	10.12	10.28	10.58	9.66	10.43
C_2H_2	0.02	0.02	0.02	0.06	0.03
C_2H_4	1.33	1.46	1.52	0.87	0.66
C_2H_6	0.17	0.23	0.15	0.31	0.77
SO_2	n/i	n/i	n/i	n/i	n/i
NO	n/i	n/i	n/i	n/i	n/i

Application of two step purification system including wet scrubber and absorber results in significant decrease of CO_2, SO_2 and NO_2 concentration that gives possibility to apply obtained gas for methanol synthesis.
After syn-gas purification it was compressed to 20 Bars and injected in methanol formation reactor. Methanol formation rate varies near 204-215 g of methanol per kg of catalyst per hour.

Table 5. Methanol formation rate for investigated source materials

	Birch	Spruce	Peat moss	Bottom peat	Brown coal
W_{Me}, $\frac{g(Me)}{kg(Cat)h}$	203.8	206.7	212.9	210.5	214.8

Then methanol was transferred into hydrocarbons synthesis reactor where it was heated to 350^0C and transferred in to dimethyl ether over γ-alumina and then dimethyl ether was transferred in to hydrocarbons over H-ZSM-5. The result presented in table 6.

Table 6. Hydrocarbons formation rate for investigated source materials

	Birch	Spruce	Peat moss	Bottom peat	Brown coal
W_{Me}, $\frac{g(C_nH_{2n})}{kg(Cat)h}$	152.9	155.0	159.6	157.9	161.1

The resulting values of obtained process characteristics are presented in table 7.

Table 7. Hydrocarbons formation rate for investigated source materials

	Birch	Spruce	Peat moss	Bottom peat	Brown coal
Liquid hydrocarb. yield, kg/kg	0.55	0.51	0.64	0.62	0.72
Energy output, MJ/kg	7.5	7.3	8.2	8.9	9.3
Energy consumpt., MJ/kg	11.1	10.6	11.9	12.8	14.1
Energy balance, MJ/kg	-3.6	-3.3	-3.7	-3.9	-4.8

The highest liquid hydrocarbons yield was found to be 0.72 kg(Hydrocarbons)/kg(initial source) for brown coal. The lowest liquid hydrocarbons yield 0.51-0.55 kg(Hydrocarbons)/kg(initial source) was found for wood residuals. Deferent types of peat characterizes by medium liquid hydrocarbons yield 0.62-0.64 kg(Hydrocarbons)/kg(initial source). For all substrates a negative heat balance was obtained. The highest values of energy needed to be inputted in the system were found to be 4.8 MJ/kg for brown coal. The lowest value of energy needed to be inputted in the system was found to be 3.3-3.6 MJ/kg for wood residuals. In all cases liquid organic phase consists of 1-7 wt. % paraffins, 1-2 wt. % olefins and 90-95 wt. % of various aromatic compounds. The composition of the liquid organic phase is not constant and varies depending on the amount of transformed methanol. An increase in the concentration of aliphatic hydrocarbons is observed during reaction. Comparison of obtained results with Fischer-Tropsch process shows some benefits in energy consumption and process operation. However due to high concentration of aromatic hydrocarbons in organic liquid fraction additional dearomatization treatment by catalytic hydrogenation is needed for application of residual liquid as a fuel.

4 Conclusion

A series of experiments for law valuable carbon sources and biomass transformation in liquid hydrocarbons were performed. Transformation process consists of four main steps including biomass transformation into syn-gas, syn-gas purification, methanol synthesis and methanol to hydrocarbons transformation process. The highest liquid hydrocarbons yield was found to be 0.72 kg(Hydrocarbons)/kg(initial source) for brown coal. The lowest liquid hydrocarbons yield 0.51-0.55 kg(Hydrocarbons)/kg(initial source) was found for wood residuals. Deferent types of peat characterizes by medium liquid hydrocarbons yield 0.62-0.64 kg(Hydrocarbons)/kg(initial source).

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