Synthetic diesel from biomass by Fischer-Tropsch synthesis

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Abstract. The production of liquid hydrocarbons fuel from biomass by Fischer-Tropsch synthesis has become more and more attractive due to its advantages compared to fossil diesel: environmental friendliness by recycling wood and agricultural wastes and reducing emissions of greenhouse gases (CO, CO_2, SO_2, NO_x, unburned hydrocarbons and particulate matters), absence of sulphur and nitrogen, higher combustion efficiency, higher cetane number and also the compatibility with existing diesel engines and infrastructure.

In this paper the Fischer-Tropsch synthesis process from biomass applied at the Güssing plant was investigated. Each stage of the installation: biomass gasification, gas cleaning and Fischer-Tropsch process, in terms of the equipment used and the parameters necessary for the synthesis, was analysed and discussed.

Also, during the synthesis the gas composition of the syngas before and after each stage was analysed, using gas chromatography. The same analytical method was used in order to determine the carbon distribution of the Fischer-Tropsch fuels obtained in the process. The ASF model was applied and an α value of 0.89 was calculated for the products.

Key words

Biodiesel, Biomass, Fischer-Tropsch synthesis, Syngas

1. Introduction

Nowadays, one of the biggest environmental problems is caused by transportation, which contributes with 21% of the greenhouse emissions in Europe and continues to grow. Road traffic is responsible for more than 90% of these emissions, generating especially CO, NO_x, SO_2, particulate matter, volatile organic compounds and other forms of pollution, due to its continuous growth during 1990-2002 [1].

The limitation of crude oil reserves, high crude oil prices, instability of the crude oil supply chain, as well as the environmental problems lead to EU legislation and strategies which put the transportation fuel sector under pressure [1] and determined the search for alternative fuels. The term biofuel is referring to liquid or gaseous fuels that are predominantly produced from biomass [2]. Among the renewable energy sources, biomass has the advantages of its availability worldwide (agricultural crops, wood, agricultural and wood wastes, municipal wastes), positive environmental properties due to lower CO_2, sulphur and nitrogen emissions, ability to provide not only liquid, but also solid and gaseous fuels [1], [2], [3]. There are different processes to decompose biomass – extraction, fermentation, thermo-chemical conversion – in order to obtain biofuels, like bioethanol, biomethanol, biohydrogen, bio-char, biogas, syngas, vegetable oils, biodiesel or Fischer-Tropsch products (diesel, gasoline, kerosene, and waxes).

In Europe, among all the biofuels produced, diesel substitutes become more and more attractive, due to the high share of diesel in the transportation fuel sector, with the advantage of high efficiency and lower emissions. There are three main ways for synthetic diesel synthesis:

- Transesterification process that uses oils to produce first generation of biodiesel;
- Hydrogenation of biooils;
- Fischer-Tropsch synthesis that uses syngas obtained by gasification of biomass in order to produce the second generation of biodiesel.

Even if nowadays, transesterification is the most used process for obtaining biodiesel, there are some disadvantages of this process that makes Fischer-Tropsch synthesis more suitable:

- only oils can be used as feedstock;
- competition between biodiesel production and food crops.
- blending rate – only blends of 7% biodiesel with petroleum diesel can generally be used in unmodified diesel engines, while in pure form (B100) biodiesel requires engine modifications to avoid maintenance and performance problems.

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Under these circumstances Fischer-Tropsch synthesis is a good alternative for the production of diesel. The main objective of this paper was to investigate the process of producing synthetic diesel from biomass by Fischer-Tropsch synthesis, applied at the combined heat and power (CHP) plant Güssing.

Another objective of this work was to optimize the composition of the syngas before and after each important stage during the Fischer-Tropsch synthesis:

- before steam reformer
- after steam reformer
- before Fischer-Tropsch
- after Fischer-Tropsch

The results obtained show the efficiency of the steam reformer on converting hydrocarbons to H_2 and CO, the efficiency of the fixed bed adsorbers on removing the sulphur compounds. Also, the products obtained in the Fischer-Tropsch process were analysed in order to calculate the α value by applying the ASF model on the products carbon distribution.

2. Experimental

A. CHP plant

The syngas used in the laboratory scale Fischer-Tropsch plant is obtained at the biomass combined heat and power plant (CHP) Güssing which uses the FICFB-gasification system (Fast Internal Circulation Fluidised Bed) developed by the Institute of Chemical Engineering of the Technical University of Vienna and AE Energietechnik. The FICFB-gasification system (Fig. 1) has two chambers: the gasification zone as a stationary fluidised bed reactor and the combustion zone as a circulating fluidised bed reactor [4] which are connected with a chute. The gasification zone is fluidised with steam, generated by the waste heat of the process, while the combustion zone is fluidised with air to deliver the heat for the gasification process via the circulating bed material [5].

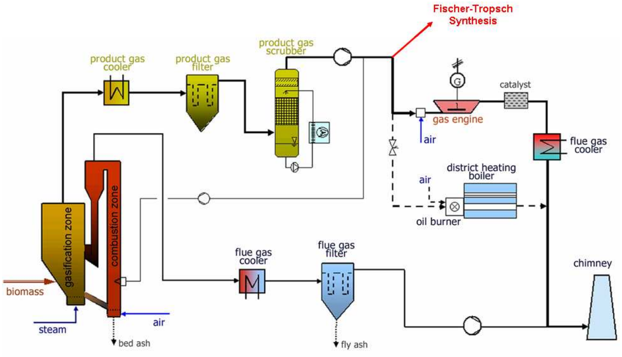

Fig. 1. Flow sheet of the CHP plant

In the first step, biomass is fed into the gasification, heated up and converted mainly into CO, CO_2, CH_4, H_2, H_2O and char. In the second step, the bed material and the remaining carbon is transported via the chute into the combustion zone, where the remaining carbon and a slipstream of the product gas is combusted. The heated bed material is then separated from the flue gas in a cyclone and fed back into the gasifier to deliver the heat for the gasification reaction.

In order to clean the syngas a two stage cleaning system is used. First the gas is cooled with a water heat exchanger from 850-900 °C to 160-180 °C and passed through a fabric filter to remove the tars and the particles. In the second stage, a scrubber with rapeseed methyl ester (RME) as a solvent is used to remove the tars from the gas. In the scrubber the gas is cooled down to about 40 °C and dried to a water content of 10Vol%. After the final cleaning stage the synthesis gas is used in a gas engine to produce electricity and heat. A small slipstream is transported to the Fischer-Tropsch plant in order to produce synthetic diesel. The characteristic data of the CHP plant Güssing [5] are:

- Fuel power – 8000 kW;
- Electrical output – 2000 kW;
- Thermal output – 4500 kW;
- Electrical efficiency – 25%;
- Thermal efficiency – 56.3%;
- Total efficiency – 81.3%.

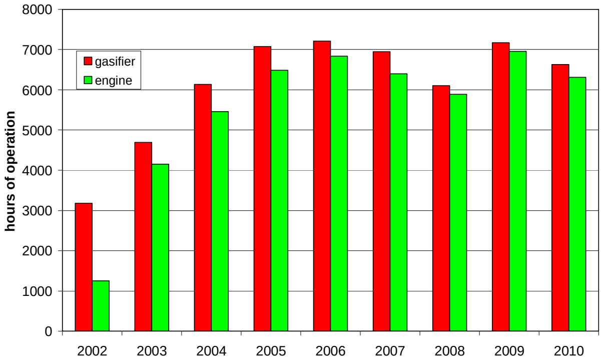

Fig. 2. Hours of operation at CHP plant Güssing

B. Fischer-Tropsch installation

The equipment used in the laboratory scale Fischer-Tropsch plant can be seen in Fig. 3.

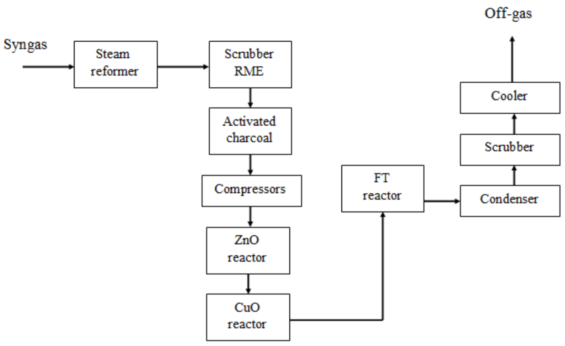

Fig. 3. Flow sheet of the Fischer-Tropsch installation

The principle of the Fischer-Tropsch reaction is represented by the following equation:

$$CO + 2H_2 \rightarrow (\text{-}CH_2\text{-}) + H_2O \qquad (1)$$

The CHP plant is delivering the synthesis gas as it is mentioned in the previous chapter. In order to make CH_4 and higher hydrocarbons accessible for the FT synthesis and to adjust the H_2/CO ratio, steam reforming is used. The H_2/CO ratio of the product gas from the CHP plant is usually 1.8:1, where as by reforming a H_2/CO ratio of 2.1:1 can be achieved [4]. The equation of the methane reforming reaction is:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (2)$$

The steam reformer was designed and optimized by Potetz et al [6] at the Technical University of Vienna. It consists of a water dosage pump to add the necessary amount of steam, two heat exchangers to preheat the syngas until 850-950 °C, two heated reforming reactors and a heat exchanger to cool down the gas before it reaches the RME scrubber used for the gas drying and cleaning. The drying stage is very important because the syngas contains an appreciate amount of water after the reformer. The scrubber cools down the syngas to about 3 °C, removing not only the water but also some aromatic compounds like naphthalene. Rapeseed methyl ester is used as solvent due to its large availability in Güssing.

The Co-based catalyst of the Fischer-Tropsch synthesis is very sensitive to small amounts of sulphur compounds which rapidly deactivate the catalyst by forming surface metal sulphides. Spath et al [7] suggested different recommendations for the maximum sulphur content in the syngas – in the development of the Fischer-Tropsch process, Fischer recommended a maximum of 4 ppm sulphur, while during time, researchers claimed that the sulphur level should be below 1 ppm or even 60 ppb. Different adsorbers are used in the laboratory scale FT plant for the adsorption of H_2S and organic sulphur compounds. The activated charcoal coated with KI acts as a catalyst to convert H_2S in elementary sulphur which is adsorbed. For the purification to ppb sulphur levels, fixed bed reactors with ZnO and CuO adsorbers are also used.

After the gas treatment, the clean and compressed gas (20 bars) enters the three phases slurry reactor designed and optimised by Ripfel-Nitsche et al [8] at the Technical University of Vienna. The reactor is a tube with a diameter of 0.1 m, a height of 2.5 m and a volume of about 20 l. During the experiments, Co-based catalyst was used. Before the start-up 2.5 kg of the reduced catalyst were suspended in 10 kg of FT-waxes and filled into the reactor. The operating conditions maintained at least for two weeks were the following:

- Temperature – 230 °C;
- Pressure – 20 bars;
- Gas flow – 5-6 Nm^3/h.

After cleaning and compression, in the previous installation equipment, the syngas enters at the bottom of the slurry reactor through a nozzle for fluidization. The syngas gets in contact with the catalyst and the CO hydrogenation takes place. On the top of the reactor a filter is placed in order to retain the catalyst and to release the Fischer-Tropsch products as well as the off-gas.

The last stage of the FT installation is the product separation and condensation, established in three steps: First a condenser is used at the same pressure but lower temperature as the FT reactor to condensate the long chain hydrocarbons and the water from the product containing gas. The gas is then expanded through two needle valves to about 80 mbar and transferred into the second step, which is the off-gas scrubber (OGS). The OGS is operated with water at 80 °C in order to prevent the packing blockage with FT waxes which were not condensed in the prior step. For product retrieval from the condensing vessel the product is led through a third needle valve into the OGS. The last step is the condensation of the short chain hydrocarbons in a cooler (OGC) where the gas is cooled down to about 5 °C by a water-glycol mixture. After the run the separated liquid and solid products are manually withdrawn, while the off-gas is sent back to the CHP plant. More details about the advantages of the FT unit are discussed in the next chapter.

C. Gas composition analysis

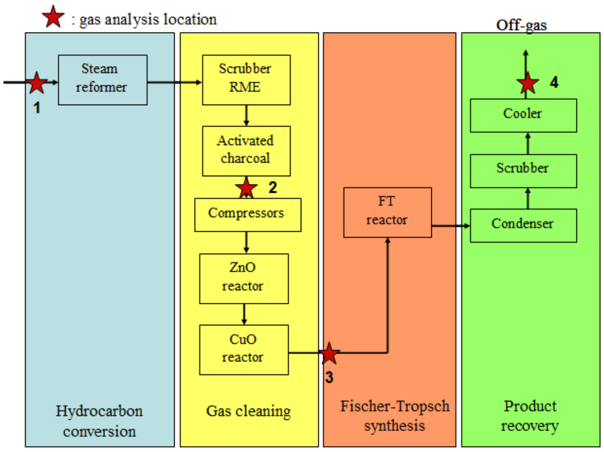

Fig. 4. Flow sheet of the gas sampling points at the Fischer-Tropsch installation

The composition of the syngas used for the Fischer-Tropsch synthesis was determined by online measurements with the gas chromatograph (GC) Clarus 500 from "Perkin Elmer". The GC was equipped with three different columns – 2 apolar and 1 mole sieve 5 Å, connected with 2 automated valves and an injection loop of 500 µl. As carrier gas helium was used. Two types of detectors were used: a thermal conductivity detector (TCD) and a flame ionization detector (FID). The concentrations of the permanent gases (O_2, H_2, CO, CO_2) were detected by the TCD, while the hydrocarbons up to carbon number 3 were analysed with the FID. The hydrogen concentration was calculated as 100 minus the sum of the gas concentration given by the two detectors. The gas analysis was made in four points of the Fischer-Tropsch installation, which can be seen in Fig. 4. The measurements were made when the installation worked continuously at the established parameters. After one week the liquid and the solid products were withdrawn and analysed.

D. Product analysis

The Fischer-Tropsch products withdrawn from the off-gas scrubber and the off-gas cooler were analysed with an Elite HT SimDist column (6 m x 0.53m x 0.15µm) on a Clarus 500 "Perkin Elmer" gas chromatograph. The samples were dissolved and diluted in CS_2 and injected by an autosampler. As carrier gas helium was used. Detection and quantification was done by an FID. To identify the peaks corresponding carbon number, samples spiked with pure components (C_{10} and C_{15}) were analysed.

3. Results and discussion

A. Installations studies

1) CHP plant

A well established gasification method – FICFB system is used by the CHP plant Güssing. Compared with gasifiers which operate with air, the FICFB-gasification system has the advantage of producing an almost nitrogen free gas ($N_2 < 2$ vol% [9]) which can be used successfully in the Fischer-Tropsch synthesis. Zuberbühler et al [10] showed that the syngas obtained by air gasification had 48% N_2, while the one produced with steam gasification had only 2% N_2. The performance of the FICFB system at the CHP plant Güssing is shown in Table I, where the typical ranges of the main components of the synthesis gas are presented.

Table I Main components of synthesis gas

Component	Range Vol - %
H_2	35-45
CO	20-30
CO_2	15-25
CH_4	8-12
N_2	1-3

The efficiency of the two cleaning stages – the fabric filter and the RME scrubber can be observed in Table II which contains the typical ranges of the undesirable components measured in the raw gas as well as in the clean gas [5].

Table II Undesirable components of synthetic gas

Component	Raw Gas	Clean gas
Tars [mg/Nm^3]	1500-4500	10-40
Particles [mg/Nm^3]	5000-50000	<5
NH_3 [ppm]	1000-2000	500-1000
H_2S [ppm]	n. a.	~ 150
Organic S [ppm]	n. a.	~ 30
HCl [ppm]	n. a.	~ 5

n. a. – not analysed

The CHP plant Güssing is not producing any liquid residue. The only solid residue is the ash from the combustion zone with very low carbon content (< 0.5 w%), being an important advantage to other gasifier concepts [5].

2) Fischer-Tropsch installation

The main equipment of the FT installation is the slurry reactor. Compared with a fixed bed reactor, in the slurry reactor the heat of the FT reaction is removed rapidly from the catalyst particles due to the liquid phase (waxes). In this way, overheating of the catalyst is avoided and thus deactivation by sintering effects cannot occur. Also, the slurry reactor has the advantage of being more isothermal, meaning it can be operated at higher average temperatures and therefore higher conversions are possible. The catalyst can be removed online, easier than in case of a fixed bed reactor or a multitubular reactor, allowing longer reactor runs [7], [11].
Fig. 4 shows the online measurements of the flow gas, the pressure and the temperature of the bottom and the top trace heating as well as the temperature obtained in the slurry. It can be observed that the FTR-slurry temperature is higher than the temperature of the trace heating which can be explained by the fact that the Fischer-Tropsch reactions are highly exothermic, indicating the activity of the catalyst. Also two breaks during the operation can be seen when the pressure in the FTR dropped under 20 bars. The pressure drops are the result of the CHP plant shut down and the Fischer-Tropsch installation operating automatically with N_2 at this time.

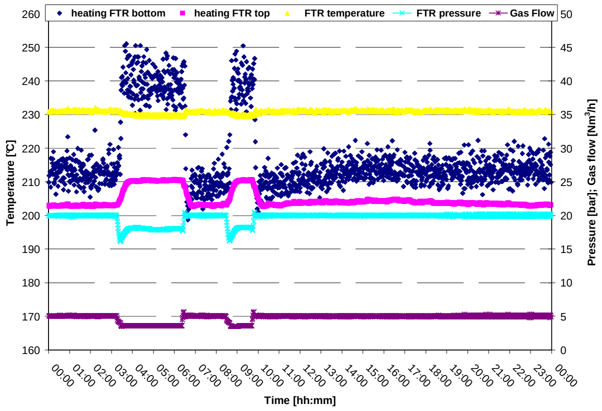

Fig. 5. Online measurements of temperature during FT operation

B. Gas composition

The gas composition measured during the continuous operation of the FT installation is presented in Table III. It can be observed, as mentioned in the previous chapter, that the N_2 concentration is very low, due to the efficiency of the FICFB-gasification system. The CH_4 concentration in the syngas entering the installation is about 10%, while after the steam reformer the CH_4 content drops to 7%. At the same time H_2 and CO concentrations are increased after the steam reformer.

These measurements, as well as the calculated H_2/CO ratio, show the efficiency of the steam reformer.
Another aspect observed is the absence of ethylene and propene after the CuO reactor. These results can be attributed to the CuO catalyst hydrogenating the alkenes and therefore increasing the content of the alkanes C_2H_6 and C_3H_8 in the syngas.

Table III Gas composition of the syngas at different stages of the Fischer-Tropsch installation

Gas Composition %	before Steam reformer **1**	after Activated charcoal **2**	after CuO reactor **3**	After Off-gas cooler **4**
H_2	39.8	48.7	48.3	37.06
CO	20.9	21.4	21.2	16.5
CO_2	21.8	19.3	20.0	29.5
N_2	2.43	2.7	2.34	3.14
CH_4	10.5	6.9	7.4	12.4
C_2H_4	3.4	0.5	0	0.02
C_2H_6	0.2	0.05	0.6	1.06
C_3H_6	0.2	0.002	0	0
C_3H_8	0.02	0.001	0.002	0.1
H_2/CO [-]	1.9	2.2	2.3	2.2
Total S [ppm]	110	3	0.003	-

C. Product distribution and selectivity

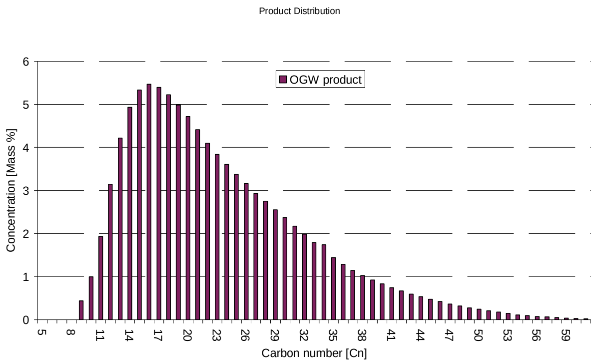

Fig. 6. Carbon distribution of the OGS product

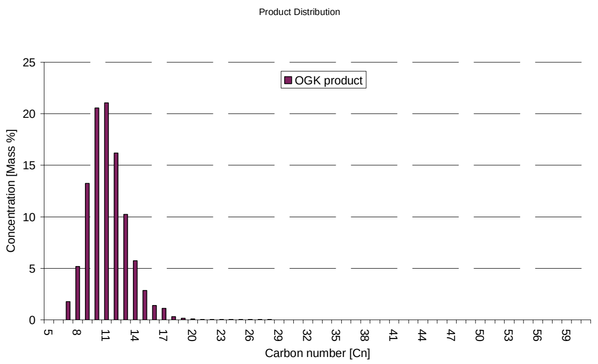

Fig. 7. Carbon distribution of the OGC product

The solid (OGS) and the liquid (OGC) products obtained in the FT synthesis at desired parameters were analyzed and the products carbon distribution can be seen in Fig. 6 and Fig. 7. In case of the OGC the maximum mass fraction is reached by C_{10} and C_{11} due to a high content of short chain hydrocarbons, while in case of the OGS the maximum mass fraction is reached by C_{15} to C_{17}, but also with important amounts of C_{20}-C_{26}. Due to the different temperatures in the two condensation steps, a different product distribution can be observed as explained already above. The typical product distribution for conventional fossil diesel lies between C_{10} and C_{20} [12]. The total carbon distribution, of the products condensed, is presented in Fig. 8. It contains hydrocarbons with carbon number starting at 7 going up to 64.

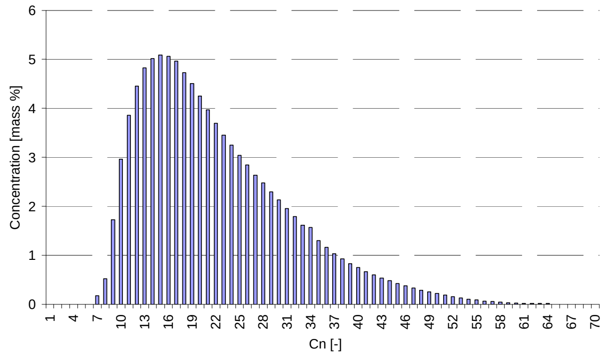

Fig. 8. Total products carbon distribution

The amount of the gaseous and the liquid products with a carbon number up to 10 that could not be completely condensed was determined by the Anderson-Schulz-Flory (ASF) plot. The ASF model represents the chain polymerization kinetics and can be expressed with the following equation:

$$W_n = n(1-\alpha)^2 \cdot \alpha^{n-1} \qquad (3)$$

where W_n is the mass fraction of the product containing n carbon atoms and α is the chain growth probability [5], [7].

For the calculation of the α value the following equations were used:

$$\log\frac{W_n}{n} = n\log(\alpha) + \log\frac{(1-\alpha)^2}{\alpha} \qquad (4)$$

$$\log\frac{(1-\alpha)^2}{\alpha} = const. \qquad (5)$$

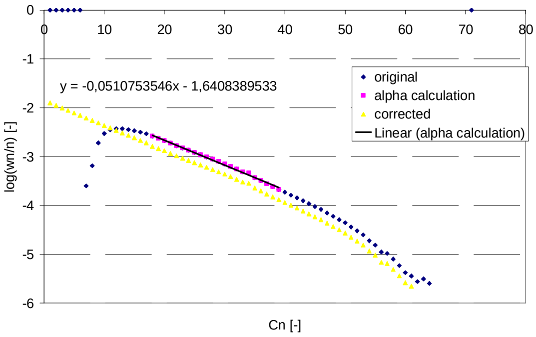

Fig. 9. ASF model for the products carbon distribution

In Fig. 9 the ASF plot of the product resulted from Fischer-Tropsch synthesis can be seen. With the equation obtained by the ASF model an α value of 0.89 was calculated. The calculation of α was done between C_{18} and C_{39}. This value is characteristic for a Co catalyst which has a typical range of α between 0.85-0.95 [13]. Applying the ASF model and the derived α value a corrected carbon distribution of the product was calculated containing the missing hydrocarbons (Fig. 10).

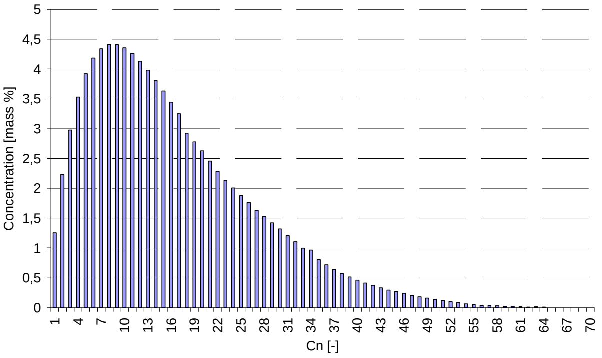

Fig. 10. The corrected products carbon distribution

4. Conclusions

The following conclusions can be drawn from the study:

- The FICFB system is a well established gasification method, producing synthesis gas with a high hydrogen and a low nitrogen content;
- The CHP plant and the FT installation have efficient cleaning stages in order to remove undesirable compounds from the syngas;
- Using the steam reformer in the FT installation, the H_2/CO ratio was adjusted from 1.9 to 2.2, while the CH_4 concentration dropped from 10% to 7%;
- Besides adsorption of sulphur compounds, CuO adsorber causes the conversion of alkenes to alkanes;
- The condensed Fischer-Tropsch products carbon distribution contained hydrocarbons with carbon number from 7 to 64;
- The derived α value of 0.89 is within the typical Co catalyst range of 0.85-0.95;

The results obtained in this study represent a starting point for the next experiments. Based on the established parameters (230 °C, 20 bars and 5-6 Nm^3/h) as a reference, a parameter variation will be done with the Co-based catalyst, which includes temperature, pressure and gas flow variation.

Acknowledgement

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