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SOLID-RECOVERED FUEL TO LIQUID CONVERSION USING FIXED BED GASIFICATION TECHNOLOGY AND A FISCHER–TROPSCH SYNTHESIS UNIT – CASE STUDY

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ABSTRACT

In order to utilise energy-rich solid waste, its liquid conversion into valuable hydrocarbon (HC) chains is one of the ways followed worldwide to decrease the oil processing and waste landfilling at the same time. The unique fixed bed updraft gasification reactor with an oscillating circular grate, situated in VŠB – Technical University of Ostrava, Czech Republic, can generate up to 90 $m^3 \cdot h{-}^1$ of CO and H_2-rich synthetic gas. Such valuable mixture is suitable for the gas to liquid conversion in Fischer–Tropsch Micro Catalyst Bed (F-T MCB) unit, where more complex substances of higher temperature and pressure form in the environment. This article focuses on solid-recovered fuel (SRF) gained as a mixture of industrial and communal waste sources. Gasification of such material in the fixed bed reactor can produce approximately 600 and 250 m^3 of CO and H_2, respectively, per ton of SRF in the abided gasification conditions. The gas, retrieved from the process, undergoes a thermochemical reaction on the surface of a catalyst within the reactor of the Fischer–Tropsch unit. As a result, a highly valued HC liquid is achieved from the suitable, non-recyclable waste treatment. Cobalt and iron catalysts in their plain form, as well as the catalysts enriched with Mn/K enhancers are put in comparison in this study. The quality and quantity of the synthesis product are examined and the technological aspects of both units are described. The amount of HC synthesis product ranges from 18 to 45 kg per ton of fuel. The composition tends to form HC chains in favour of groups of alcohols and alkanes.

Keywords: cobalt catalyst, Fischer–Tropsch synthesis, fixed bed reactor, gasification, iron catalyst, solid-recovered fuel, waste management.

1 INTRODUCTION

Ever-growing waste disposal is one of the most discussed issues globally. Upcoming European regulations are forcing many nations to cease landfilling, and new waste treatment methods and solutions are, therefore, necessary. In 2018, in the area of densely populated region of Ostrava, Czech Republic, approximately 136 kt of waste was generated, out of which 39 kt (28%) was energetically or materially utilised and 93 kt (68%) was placed in the adjacent landfill [1].

The waste disposal company *Waste Collection and Utilisation (OZO – Ostrava)* possesses the facility to partially utilise these wastes and form a solid mixture of non-recyclable, energy-rich material. With other transregional sources taken into the count, OZO – Ostrava generated 30 kt of solid-recovered fuel (SRF) in 2018. Such material of appropriate bulk density and granulometry can serve as a proper fuel for gasification technology.

This thermochemical process decomposes organic substances contained within the fuel. As a result of this reaction, the product of the process – the producer gas – is formed. This gas contains H_2, CO, CO_2, C_nH_m, H_2O and N_2, along with tar compounds and inorganic components. With suitable gas treatment, it is possible to acquire synthetic gas with an appropriate content of H_2 and CO for the catalytic liquefaction in the Fischer–Tropsch (F–T) technology.

The reactor of F–T unit is filled with active catalytic substances impregnated on spherical bearer made of alumina (Al_2O_3). The active substances used for the purposes of this study are

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cobalt and iron. The properties of their pure form and their combinations are observed on the application of SRF-generated synthetic gas. Mn and K are often used in the catalytic problematics in order to enhance the synthesis efficiency [2]. In this study, Mn/K-enriched Fe is examined.

2 MATERIALS AND METHODS

2.1 Fuel

The OZO – Ostrava fuel, PALOZO II (Palivo OZO – OZO fuel), represents a solid mixture of industrial and municipal waste collected in the area of Ostrava city and its surrounding dwellings. The main content share of this fuel is dominated by non-recyclable plastic, paper, wood and textile materials. The composition of the waste content is shown in Table 1. The results given represent only a range of values as the real numbers vary with each delivery [3].

This material mixture undergoes an intensive treatment which includes drying, shredding, milling, separation and homogenisation. The calorific value of the product usually exceeds 20 $MJ \cdot kg^{-1}$. The moisture content is below 15% and ash fraction up to 10%. Particle size ranges between 1 and 20 mm. Its shape is best described as fine shreds. Also, the separation of materials with high content of sulphur and chlorine is essential. The presence of these elements and their compounds is strictly below 0.5% and 1% of the total content for chlorine and sulphur, respectively [3, 4].

This fuel, as well as source materials, is periodically sampled and analysed in the laboratory to check the quality and chemical and physical properties, before it is used for commercial purposes. The PALOZO II fuel shreds are shown in Fig. 1.

Table 1: Illustrative composition of PALOZO II fuel [3].

Plastics	**Paper**	**Wood**	**Textiles**	**Other**
(%)	(%)	(%)	(%)	(%)
40–70	20–40	0–30	0–30	0–10

Figure 1: PALOZO II fuel [4].

2.2 SRF gasification

The most important thermochemical reactions with respect to quantity and quality occur within the body of the gasification reactor. In the case of Energy Research Center (ERC) application, the fuel is delivered above the circular grate through its middle by a pair of screw conveyors, one horizontal and the other vertical. After ignition, the reactor is heated up to the gasification temperature, and during the whole process, the temperature is secured by a partial combustion of the fuel itself. Therefore, the reactor is autothermal, that is, without outer heating source [5].

The lowest limiting temperature for PALOZO II gasification is 750°C. Below this temperature, the necessary decomposition reactions cannot occur sufficiently. An upper temperature limit (900°C) is given by the calorific value of the fuel itself. The pressure conditions within the reactor are held around 0.1 kPa below the atmospheric pressure during the measurements, which secures the updraft suction of the producer gas.

In this experiment, the gasification conditions were based on a previous research concerning the problematics of this specific fuel [4]. The best conditions in terms of conversion efficiency were defined as: 800°C was the gasification temperature with 0.1 kPa below the atmospheric pressure, the fuel feed value was approximately 9.4 $kg{\cdot}h^{-1}$ and the oxidiser (air) suction rate was equal to 60 $m^3{\cdot}h^{-1}$. The producer gas flow in this experiment was equal to 40 $m^3{\cdot}h^{-1}$ on average, which was secured by a suction ventilator at 2,500 rpm.

The equipment of the gasification reactor includes a hot particle filtration unit with filtration candles to capture solid particle pollutants, a pair of coolers attached to a tar condensate collection vessel, a suction ventilator and a burning chamber for unused producer gas destruction, as seen in Fig. 2. All the components are connected with a refractory pipeline, equipped with several sampling points and temperature, pressure and flow indicators [5].

During the process, a gas sampling is usually done right behind the reactor and analysis with Pollutek 3000p gas composition analyser is run online. The information of gas chemical composition immediately evaluates the quality of the process. Prior to the analyser, the gas flows through a sampling train consisting of ice-cooled impinger bottles where pollutant collection is possible following the ‘tar protocol’ standards [6].

2.3 F–T synthesis

The gas feed is realised by several equipped closing valve gas inlets. The reaction gases get mixed afterwards and flow through the electric preheater. The preheater is set at 200 °C. Increased temperature supports the chemical reaction and results in better efficiency of the

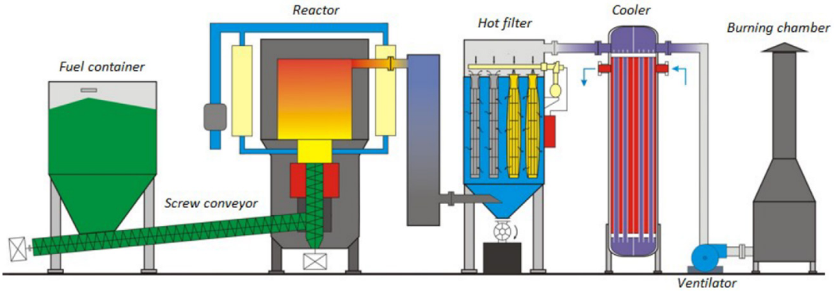

Figure 2: ERC gasification technology [7].

process. The optimal temperature conditions for the catalytic reaction are often defined as: 200°C–320°C, dependent on other factors [8, 9].

The catalytic reactor, placed in the electrical furnace, follows after the preheater. Its shape is cylindrical and it is proportionally much smaller than the gasification reactor. Its inner diameter is 10 mm and length is 100 mm. Therefore, only a part of the producer gas can be fed into F–T Micro Catalyst Bed (MCB). Due to insufficient chemical composition rate of the synthetic gas, an additional H_2 source has to be attached to reach the desired mass rate. Gases can be fed into the technology from separate bottles, if necessary. The reactor is filled with 3:1 (mass) mixture of catalyst/inert SiO_2 with additional 0.5 g of inert at the bottom and the top of the reactor, for better temperature profile equality. The total reactor load is 5 g.

Below the reactor is one of two separator modules, where heavier synthesis products (predominantly alkanes >C9) get separated from the flow and are drawn from the system periodically. The second module follows to separate the rest of the lighter liquid fraction (predominantly C5–C7 alcohols along with the rest of alkanes) from the remaining gas. This module is equipped with a cooling fan to ensure sufficient condensation and separation of the synthesis product. The residual off-gas flows through a flow meter and Pollutek 3000p gas composition analyser. The scheme of F–T MCB unit is depicted in Fig. 3.

During this experiment, an exact amount of 3 g of catalytic substance was exposed to a flow of pure hydrogen for a period of 4 h in increasing temperature environment. The temperature increase rate was set at 1°C·min^{-1} up to the ultimate temperature of 400°C. This phase is called catalyst activation and it supports its surface activity [10]. Steady cooling using pressurised air followed, and once the inner temperature of the reactor reached 200°C, it was increased again in a pressurised environment and the feed gases valves were opened. At this point, the synthesis began.

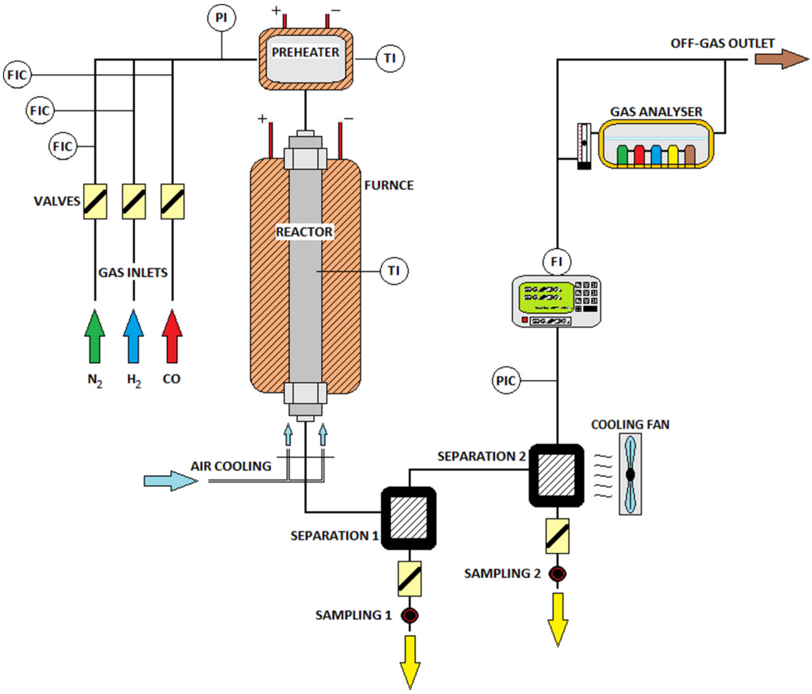

Figure 3: F–T MCB scheme.

Table 2: Chemical composition of the catalysts.

Label	**Al_2O_3**	**Co**	**Fe**	**Mn**	**K**
	(%)	(%)	(%)	(%)	(%)
Co	85	15	0	0	0
Fe	85	0	15	0	0
Co/Fe	85	7.5	7.5	0	0
Fe/Mn/K	80	15	0	4	1

2.4 Catalysts

In order to find the most suitable solution for coupling gasification and F–T synthesis units, several catalysts were designed and examined from the technical and economical point of view. Co and Fe were chosen as active catalyst substances. These represent widely used solutions for the actual commercial use [9]. All tested catalysts were impregnated on an Al_2O_3 base by series of solution impregnation. The alumina bearer was of spherical shape having pores of 1 mm diameter. The source salts of the active substances were cobalt nitrate hexahydrate $Co(NO_3)_2{\cdot}6H_2O$, iron nitrate nonahydrate $Fe(NO_3)_3{\cdot}9H_2O$, manganese nitrate tetrahydrate $MnN_2O_6{\cdot}4H_2O$ and potassium nitrate KNO_3. The mass percent of the chemical composition is presented in Table 2.

For all these catalytic solutions, alkanes are the dominant hydrocarbon (HC) category present in the synthesis product, followed by the alcohol fraction. Simplified chemical reaction occurring on the catalytic surface can be described for alkane formation as:

$$\left(2n+1\right)H_2+nCO\rightarrow C_nH_{2n+2}+nH_2O \tag{1}$$

and analogically for alcohol formation as:

$$2nH_2+nCO\rightarrow C_nH_{2n+2}O+\left(n-1\right)H_2O \tag{2}$$

Side reactions occur during the synthesis, such as water gas shift, Boudard reaction and other undesired reactions, which negatively affect the quality and efficiency of the process and durability of the catalyst [2].

3 RESULTS AND DISCUSSION

3.1 Results

A series of measurements for solid residual fuel (SRF) gasification as well as for different catalysts used in F–T synthesis were carried out in this case experiment. The industrial/municipal mixture waste (PALOZO II) was used as fuel for the gasification process in the ERC fixed bed reactor. The quality and quantity of the producer gas were monitored in order to be used in F–T synthesis technology. The production of H_2 and CO was 220 and 650 kg, respectively, per ton of PALOZO II fuel. This gas mixture was used in the synthesis reactor. Several catalysts were applied in order to define the most suitable solution for this case from economic and efficiency points of view. The catalysts were Co, Fe, Co/Fe impregnated together, Co+Fe as separate particles and Mn/K-enriched Fe.

Table 3: Experiment parameters.

Catalyst	**Test time**	**H_2**	**CO**	**Pressure**	**Temp.**	**Liquefaction**	**Conversion**
	(h:min)	**(l)**	**(l)**	**(bar)**	**(°C)**	**(%)**	**(kg_{HC}/t_{fuel})**
Fe	02:55	40.8	23.3	20	250–300	7.1	18.2
Fe/ Mn/K	02:44	37.3	21.3	20	250–300	8.1	19.8
Co	02:54	40.6	23.2	20	250–300	18.6	45.7
Co+Fe	02:57	41.3	23.6	20	250–300	16.2	40.0
Co/Fe	02:52	40.1	21.4	20	250–300	17.9	43.1

In the total time period of around 170 min for each test, approximately 14 $l \cdot h^{-1}$ of H_2 (activation excluded) and 8 $l \cdot h^{-1}$ of CO were spent. The detailed measurement values are summarised in Table 3.

The liquefaction number gives information on how much of the synthetic gas is transformed into liquid substances (mass rate). This parameter was calculated as:

$$L = \frac{X_l + X_h}{V_{H_2} \cdot \rho_{H_2} + V_{CO} \cdot \rho_{CO}} \cdot 100 \tag{3}$$

where L is the liquefaction rate, X_l the amount of light fraction collected, X_h the amount of heavy fraction collected, V_x the gas volume and ρ_x is the gas density.

The value calculated by eqn (3) serves as a quick comparison factor, set immediately after the experiment, before other analyses are managed.

Of the tested catalysts, pure Co showed the best reaction efficiency in terms of quantity. However, the economic point of view suggests significantly lesser initial costs if Co content is diminished. Taking this into consideration, Co and Fe catalysts applied together appear to be a very suitable solution for this case with 11% less productivity if mixed and only 5% if impregnated on the bearer together. As predicted, the application without Co diminishes material cost; however, the reaction is not sufficient enough in the case of pure or Mn/K-enriched Fe.

The synthesis process was not total and the off-gas contained, apart from unreacted synthetic gas, other substances also such as CO_2, methane or higher gaseous HCs in all cases. This is an indicator of insufficient chemical reaction within the reactor. Moreover, the Carl–Fischer titration analysis showed approximately 70% presence of water within the liquid synthesis samples. The carbon conversion (the sum of carbon of the output except for unreacted CO to the amount of carbon in the CO input) was above 90% for each of the tested catalysts.

The overall conversion, C_{HC}, from the source waste fuel to the pure HC synthesis product reaches up to 45 kg for cobalt applications and 20 kg for cobalt-free applications. The degree of conversion is relative to the ton of fuel and is calculated as:

$$C_{HC} = \frac{\dot{V}_p \cdot CO_{\%} \cdot m_{HC}}{\dot{m}_{wf} \cdot V_{CO}} \cdot \left(1 - W\right) \tag{4}$$

where C_{HC} is the overall fuel to product conversion degree, $\dot{V}_p$ the producer gas flow, $CO_{\%}$ the CO share in the producer gas, m_{HC} the produced liquid mass, $\dot{m}_{wf}$ the input waste fuel mass, V_{CO} the CO volume used for the synthesis and W is water in the product.

In all cases, the main products of the synthesis were represented by alkanes with peak occurrence usually between pentadecane (C15) and nonadecane (C19), and by alcohols with peak occurrence close to 1-penthanol. The Quantitative chromatography analyses were performed by a partner research institution of Wroclaw University of Science and Technology, Poland. The samples of the analyses results are shown in Figs. 4–9.

3.2 Discussion

The results presented in this case study are characteristic of a short-term experiment where both processes, gasification and F–T synthesis, ran on a full-day basis. In case of commercial use, several factors, typical for a long-term procedure, must be taken into consideration. Such factors are reliability of the gasification unit, continuous gas transport, service life of the catalysts and their efficiency vs. exposition time, catalyst poisoning, etc.

Also, the experiment has shown several ways to improve the cooperation in the future. The producer gas includes many gases apart from those needed in the synthesis, such as methane,

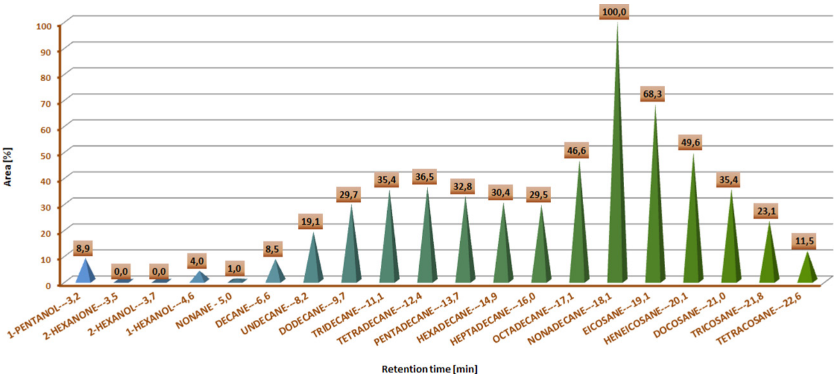

Figure 4: Fe – heavy fraction sample.

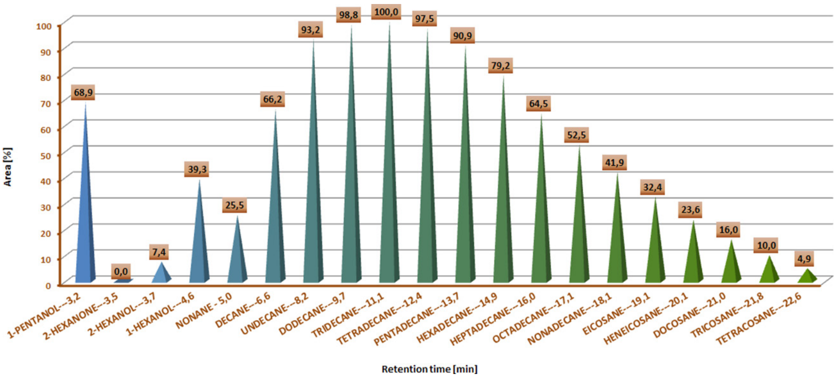

Figure 5: Fe – light fraction sample.

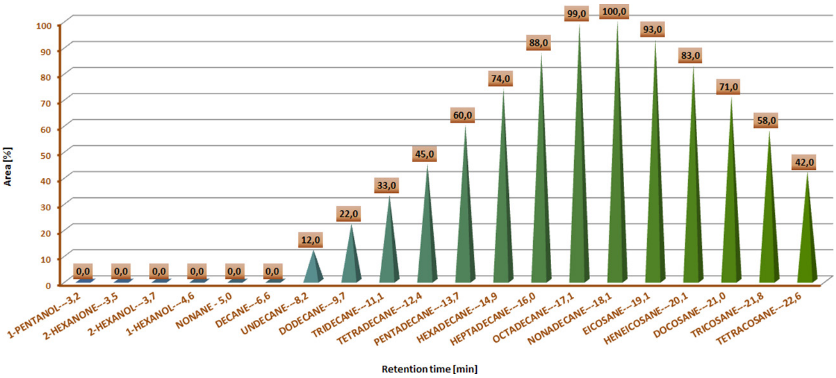

Figure 6: Co – heavy fraction sample.

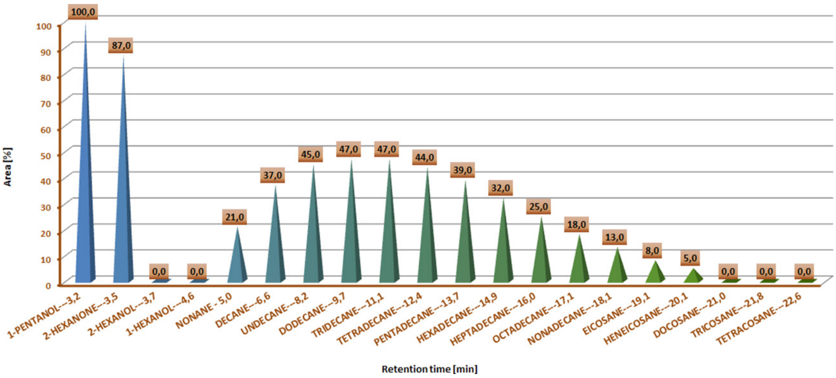

Figure 7: Co – light fraction sample.

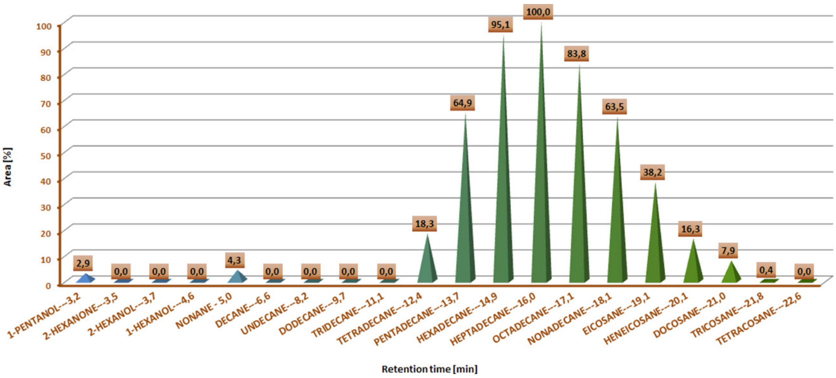

Figure 8: Co/Fe – heavy fraction sample.

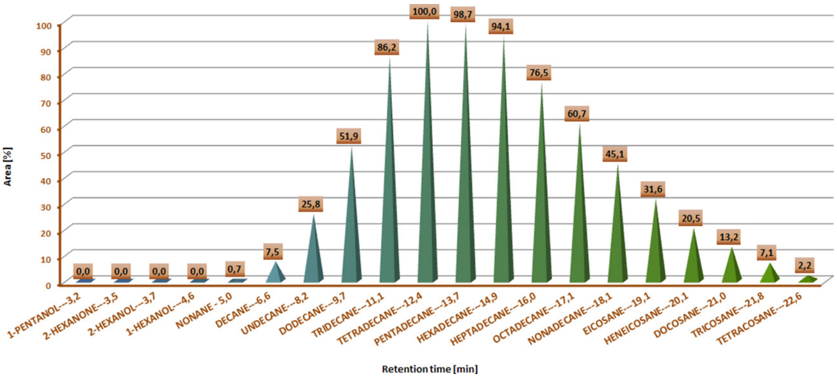

Figure 9: Co/Fe – light fraction sample.

H_2O and CO_2. The effect of the other gases on the synthesis process should be examined and should become a subject of future studies. Another problem is that of H_2/CO rate not being too close to the desired rate of 2:1, which is often presented in the literature as a ‘sweet spot’. This rate could be adjusted by modification of the gasification conditions, as well as the character of input fuel. For instance, torrefied biomass has a positive effect on higher H_2 occurrence in the producer gas.

An important consideration is that of polluting substances. The process of gasification is adjoined with several aspects which are not desirable. One of these is pollutant formation, namely, solid, dust particles and tar compounds, which represent the main issue for sufficiency of the technology.

Waste material gasification can be considered as a very specific one, where materials, although in the same category, can vary greatly. This results in different forms and quantities of pollutants produced as well. In case of PALOZO II, several experiments were done prior to this research, in order to quantify the amount of pollutants and verify the utilisation of this fuel in fixed bed gasification reactor. The results show significant presence of both pollutant categories compared to, for example, wood biomass fuel. However, the utilisation and operation were successful even with less clean conditions. Table 4 summarises the pollutant presence within the producer gas for the specific gasification conditions of PALOZO II SRF.

Although the results have shown the relative suitability of each catalyst application for waste produced synthetic gas, real applications may differ according to the desired character of the final product. More detailed analyses and measurements shall be carried out in the future in order to justify this part of the experiment.

Table 4: Average results of the comparing pollutant analyses.

Gasification temperature	**Gas humidity**	**Solid particles**	**Tar compounds**	**Gas flow**
(°C)	(%)	($mg \cdot m^{-3}$)	($mg \cdot m^{-3}$)	($m^3 \cdot h^{-1}$)
800	3.55	28,575	1819	40

4 CONCLUSION

In this coupled experiment, conducted in ERC, Ostrava, Czech Republic, fuel conversion using gasification and F–T synthesis technologies was performed. The economic and efficiency point of view was considered in this case study. The inspected input fuel, the so-called PALOZO II, was a dry mixture of non-recyclable industrial and municipal waste. The dominant composition of this fuel is represented by plastics, paper and textiles. The quantitative and qualitative aspects were examined as the waste fuel underwent the two-step solid to liquid conversion.

The results of the conversion were inspected using five various catalysts of Al_2O_3 base and impregnated active substances of Co, Fe, their combination (separate particles and simultaneous impregnation) and Fe enriched with Mn and K elements in order to enhance the synthesis reaction efficiency and quality.

The syntheses results show that the catalyst with Co, impregnated simultaneously with Fe, on the alumina bearer can process the synthetic gas with 17.9 liquefaction rate, which corresponds to an overall mass conversion rate of 43.1 kg of the synthesis product to a ton of fuel. This is a much welcomed result from the economic point of view, considering significantly lower initial and operating costs with only 6% less produced HC liquid per ton of fuel, compared to a pure Co solution.

The case of both pure Fe and Mn/K-enriched Fe is a significantly less-productive option as iron alone behaves as a weak synthesis reactant, compared to cobalt. The relative production of HC liquid per ton of fuel was 19.8 and 18.2 kg in case of enriched Fe and pure Fe, respectively. The quantitative chromatography analyses revealed the peak concentration of the HC product for alcohol fraction in 1-pentanol (C5) and for alkane fraction between pentadecane (C15) and nonadecane (C19).

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