

Scientific paper

# Multi synthetic fuel products production from waste and flue gas using the carbon effect technique

Anita Kovač Kralj,<sup>1,\*</sup> Tina Kegl<sup>2,\*</sup><sup>1</sup> Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova 17, Maribor, Slovenia<sup>2</sup> School of Science, University of Nova Gorica, Vipavska 11c, Ajdovščina, Slovenia\* Corresponding author: E-mail: anita.kovac@um.si  
tina.kegl@ung.si

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## Abstract

The usage of fossil fuels and accumulation of waste into landfills have a negative effect on the environment and generates climate changes. Waste and flue gas conversions into multi alternative synthetic fuel products and energy have the potential for CO<sub>2</sub> emission reduction by using the complete circular economy and the carbon effect technique. The novelties of this study include the carbon effect technique, which predetermines the amounts of products' production and energies' heat flows, dependent on the carbon amount, into raw materials, and predetermined carbon conversion into CO and CO<sub>2</sub>. This technique also contains a simpler mathematical model for predetermining the amount of different synthetic fuel products' production using the same raw material and process units. The individual synthetic fuels with different addition amounts can also be used as a new fuel mixture.

This approach is illustrated by the multi alternative production of synthetic fuel productions, such as methanol, ethanol and gasoline, by using MSW and flue gas, and the carbon technique, which can reduce CO<sub>2</sub> emissions by 3.5 10<sup>6</sup> kmol/a.

**Keywords:** waste gasification; flue gas; syngas; carbon; circular economy; synthetic fuels

## 1. Introduction

The global amount of municipal solid waste (MSW) placed into landfill has been rising steeply, and therefore they must use it as raw materials. The co-gasification of MSW as conversion technologies can generate useful sustainable products, such as ethanol, synthetic gasoline, methanol and other co-products and energy by using gasification, plasma, etc.

Many researchers pay a lot of attention to gasification systems. Messerle and researchers presented the thermodynamic analysis and experiments on the gasification of biomedical waste in a plasma reactor. The calculations have shown that the maximum yield of synthesis gas in the waste plasma gasification in the air and steam medium was achieved at a temperature not higher than 1600 K.<sup>1</sup> Pan et al. presented a hybrid design that combined waste gasification and coal-fired power generation, which has been proposed for improving the waste-to-energy process. In the integrated scheme, municipal solid waste is fed into the plasma gasifier and converted into syngas, which is pre-cooled by the feedwater of the coal power plant, and then

conveyed directly into the coal-fired boiler for combustion.<sup>2</sup> Lam et al. developed the two-stage optimisation model macro- and micro-stage. The micro-stage involves the optimisation and allocation of waste (e.g., biomass, industrial waste, etc.), as well as the design of an integrated processing hub. Meanwhile, the macro-stage handles the synthesis and optimisation of the waste-to-energy supply network.<sup>3</sup> Cucchiella et al. presented a strategy analysis of the amount of waste required to incinerate with energy recovery, considering different approaches based on unsorted waste, landfilled waste and separated collection rate, respectively. Consequently, the sustainability of a WTE (Waste to Energy) plant is evaluated as an alternative to landfill for a specific area.<sup>4</sup> Diyoke et al. developed a gasification model in Matlab to simulate a downdraft gasifier using wood as the feedstock. The downdraft gasifier was divided conceptually into three zones: The pyrolysis zone, the combustion/oxidation zone and the reduction zone.<sup>5</sup> Behrend and Krishnamoorthy explored alternatives to landfilling using a multi-criteria decision-making model and a linear optimisation model. This process ranked the gasification alternatives using various criteria, and deter-

mined that steam gasification was superior to the other options, due to its capacity and clean by-product gases.<sup>6</sup> Nguyen and co-workers investigated the characteristics of the residues after gasification of bagasse pellets in a semi-industrial scale gasifier, and their potential for use as CO<sub>2</sub> adsorbents.<sup>7</sup> Okati et al. developed a computational model to evaluate the plasma gasification process of polychlorinated biphenyl wastes. The model was created in the Aspen Plus® commercial software.<sup>8</sup> Barontini et al. presented the co-gasification of woody biomass with organic and waste matrices in a down-draft gasifier. The model was calibrated with the experimental data, and proved to fit the syngas composition and physical properties with satisfying accuracy.<sup>9</sup> Chanthakett et al. researched a critical assessment of waste to energy gasification technology for the municipal solid waste (MSW) on processing, energy recovery, environmental performance and economic perspectives, including both the explored and identified suitable simulation tools for optimising the gasification.<sup>10</sup> Saif et al. developed an innovative method to produce high-quality syngas for converting into aromatic hydrocarbons by using the co-gasification of biomass and plastic waste, including advanced reactor designs, fine-tuning the process parameters and developing robust catalysts.<sup>11</sup> Hasanzadeh and co-workers proposed the gasification of polyethylene waste using Gibbs free energy minimisation and the Lagrange method of undetermined multipliers. A central composite design was employed, to assess and optimise the polyethylene waste gasification. The findings revealed that hydrogen production was improved significantly by 48% by raising the steam to polyethylene waste ratio according to the water–gas shift and reforming the reactions. The hydrogen production and exergy efficiencies were enhanced by increasing the temperature.<sup>12</sup> Hasanzadeh and Azdast presented new studies in the field of Machine Learning utilisation on air gasification of polyethylene terephthalate (PET) waste, which are of the utmost importance, and can contribute to solving the environmental challenges associated with PET waste, while also promoting the development of advanced technologies in the fields of Waste Management and Renewable Energy.<sup>13</sup> Hasanzadeh et al. obtained new research of the comparative performance analysis of a wide range of prevalent plastic waste types utilising multi-criteria decision-making techniques. This study uses the “technique for order preference by similarity to the ideal solution” (TOPSIS) and grey relational analysis (GRA), and presents a thorough sensitivity analysis.<sup>14</sup>

From syngas can be produced synthetical ethanol. Chen et al. presented the novelties of temperature programmed surface reaction (TPSR), including how an Fe promoter suppressed methanation activity over Rh-based catalysts with the modified SBA-15 as support during direct ethanol synthesis of ethanol from syngas.<sup>15</sup> Liu et al. researched the study of reducibility, acidity and the basicity of the supports influenced the catalytic activity and the

product distribution for the synthesis of ethanol from syngas over Rh-based catalysts greatly. Rh particles supported on neutral or acidic supports formed the mixture of C<sub>2</sub>-oxygenates as the main oxygenated products, and Rh particles supported on basic supports formed mixed alcohols as the main oxygenated products.<sup>16</sup> Berger et al. researched the technical feasibility of the conversion into ethanol and syngas from biowaste and CO<sub>2</sub>. The producing of both products’ productions were analysed with tools such as SuperPro Designer, MS Excel and GaBi for the Life Cycle Assessment (LCA).<sup>17</sup>

Synthetic gasoline and other fuels are produced from syngas, too. Javed et al. presented new research of the high CO<sub>2</sub> selectivity of Fe-based Fischer-Tropsch microcapsule catalysts for gasoline production. The novelties of this research were the included Silicalite-1 shell, which turned the Fe/ZSM-5 core’s surface hydrophilicity to hydrophobicity, the hydrophobic nature of the silicalite-1 layer’s decreased water-gas shift reaction’s kinetics and CO<sub>2</sub> selectivity. All the zeolite supported Fe-based catalysts showed significantly high gasoline range hydrocarbons’ selectivity (about 60%).<sup>18</sup> Li et al. presented the novelties of the HZSM-5/MnAPO-11 composite and the catalytic synthesis of high-octane gasoline from syngas in flow-type fixed-bed reactors, including the highest gasoline yield. The HZSM-5/MnAPO-11 composite was prepared via hydrothermal synthesis, and the catalytic synthesis of high-octane gasoline from syngas was studied in flow-type fixed-bed reactors.<sup>19</sup> Lopez et al. reviewed the main thermochemical routes, and analysed them for the valorisation of waste polyolefins to produce chemicals and fuels. Amongst the different strategies, pyrolysis has received greater attention, but most studies are of a preliminary character. Likewise, the studies pursuing the incorporation of waste plastics into refinery units (mainly fluid catalytic cracking and hydrocracking), have been carried out in batch laboratory-scale units. Another promising alternative to which great attention is being paid is the process based on two steps: Pyrolysis and in-line intensification for olefin production by means of catalytic cracking or thermal cracking at high temperatures.<sup>20</sup>

Methanol can be synthesised from syngas, too. Puig-Gamero and co-workers used Aspen Plus® for modelling methanol synthesis from synthesis gas obtained through pine biomass gasification.<sup>21</sup> Tungalag and researchers described the gasification of municipal solid waste for synthesis gas production, including a simulation using Aspen Plus®. Their research was based on synthesis gas production using pyrolysis and plasma gasification, but not methanol production.<sup>22</sup> Li and co-workers presented a steady-state model of converting coke oven gas to methanol using Aspen Plus simulation, based on the requirements of the critical safety instrumented function.<sup>23</sup> Borgogna and researchers described methanol production from refuse derived fuel, including the influence of feedstock composition on the process yield through gasifica-

tion analysis.<sup>24</sup> Tan et al. presented the study of the Ni/CeO<sub>2</sub>/HT catalyst designed for high activity and long-term stability, by leveraging the Ce redox cycle and strong interactions between Ni-CeO<sub>2</sub> and hydrotalcite (HT) for methanol synthesis from syngas.<sup>25</sup>

The presented research is a continuation of research that was published in this journal.<sup>26</sup> The first research confirmed the simulated constant conversion of synthesis gas from different wastes of unsorted to sorted, which was the basis for this continued research. An Aspen plus® simulator, with the specific simulated chemical kinetics and process units, comes very close to the real data. This study presents the carbon conversion effect into CO and CO<sub>2</sub> by using the same raw material and process units for multi synthetic fuels, such as methanol, ethanol and gasoline products' production. The raw materials include sorted municipal solid waste and purified flue gas. This carbon conversion technique also contains a simpler mathematical model for predetermining the amount of different synthetic fuel products, which are based on the real and simulated data given with the Aspen Plus® simulator. This method has the potential to produce individual products, or even various mixtures from these basic products.

## 2. The carbon effect technique

The reuse of waste has received considerable critical attention, due to the reduction of municipal solid waste (MSW) in landfills by using the extracting of some useful materials and the further gasification of useless waste. The basic purpose of waste gasification is waste converted into different synthetic fuels' production and energy. This study presents the carbon effect technique, which is based on the input carbon content into MSW. The carbon amount can be converted into a predicted amount of CO and CO<sub>2</sub>. This

technique includes a mathematical model for alternative multi synthetic fuels' production and energy, including real and simulated data using the Aspen Plus® simulator, with the specific simulated chemical kinetics, such as Grayson, and reactors units such as RGibbs for syngas production, and REquil for fuels' production, as only these provide data that are closest to reality.<sup>26</sup> The alternatives for different synthetic fuels' production use the same waste raw material for syngas production during combustion and reforming units, presenting as the first part of the flow-diagram (Fig. 1). After syngas production take place their cooling, condensate removing and compressing, by using the same process units such as the second part of the flow-diagram. The third part includes the different reaction units for the predetermined amounts of the different products' production by using the basic specified products and energies' parameters. After the reaction, the separation and purification of different synthetic fuel products take place by using the same process units (4. Part). The different synthetic fuels are stored into different tanks (5. Part) and they can also be mixed into the new fuel product with new characteristics (6. Part).

### 2. 1. The first part – The mathematical model of the syngas production

The first part includes the equations of syngas production from the sorted MSW (as components of C and H<sub>2</sub>), which contains mostly plastics. The input carbon molar flow rate ( $F_{in,C}$ ; Eq 1) and constant carbon conversion into CO and CO<sub>2</sub> ( $X_{CO} = 0.969$ ,  $X_{CO_2} = 0.031$ ) are the basic parameters' characteristics for predetermination of the syngas composition. All the simulated constant conversions are determined by using the Aspen Plus® simulator, which were confirmed with real data. Syngases (as compo-

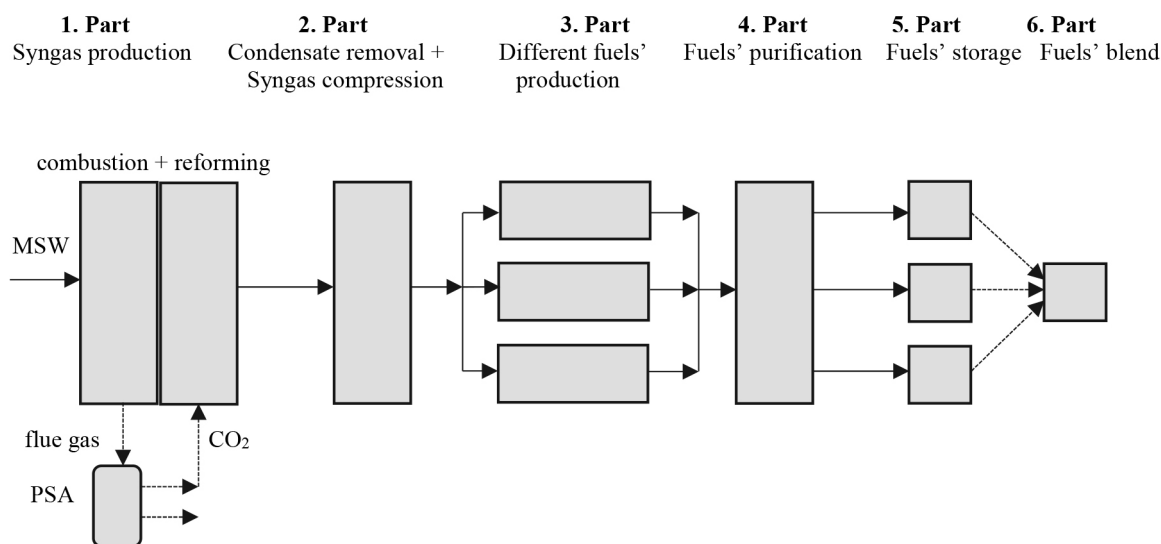
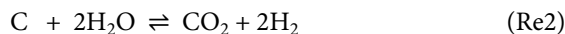
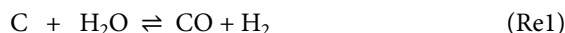


Figure 1: Flow-diagram of the carbon effect technique.

nents of CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O) are formed by the simplified reactions 1 and 2 (Re1, Re2). The output molar flow rates of CO and CO<sub>2</sub> ( $F_{\text{out,CO}}$ ,  $F_{\text{out,CO}_2}$ ) can be calculated by using Equations 2–3.



$$F_{\text{in,C}} = F_{\text{out,CO}} + F_{\text{out,CO}_2} \quad (1)$$

$$F_{\text{out,CO}} = X_{\text{CO}} \cdot F_{\text{in,C}} \quad (2)$$

$$F_{\text{out,CO}_2} = X_{\text{CO}_2} \cdot F_{\text{in,C}} \quad (3)$$

During the combustion of sorted MSW a lot of CO<sub>2</sub> emission takes place ( $F_{\text{in,cir}}$ ; Eq 4), which can be purified by using a PSA column and circulated back into the reformer (cir = Y; Fig 1), where part of the CO<sub>2</sub> reacted into CO ( $F_{\text{out,CO,cir}}$ ; Eq 5) with constant conversion ( $X_{\text{CO,cir}} = 0.7$ ), and the rest enlarged the amount of CO<sub>2</sub> ( $F_{\text{out,CO}_2,\text{cir}}$ ; Eq 6) into syngas, which has been checked into a real process.<sup>26</sup> Because of the amount of CO<sub>2</sub> circulation into reforming, the amounts of CO and CO<sub>2</sub> can be enlarged into syngas.

$$F_{\text{in,cir}} = F_{\text{out,CO,cir}} + F_{\text{out,CO}_2,\text{cir}} \quad \text{cir} = \text{Y} \quad (4)$$

$$F_{\text{out,CO,cir}} = X_{\text{CO,cir}} \cdot F_{\text{in,cir}} \quad \text{cir} = \text{Y} \quad (5)$$

$$F_{\text{out,CO}_2,\text{cir}} = F_{\text{in,cir}} - F_{\text{out,CO,cir}} \quad \text{cir} = \text{Y} \quad (6)$$

The syngas production can take place without (cir = N), or with the circulation (cir = Y) of CO<sub>2</sub> emission, which circulation can increase the amounts of components into syngas, such as CO, CO<sub>2</sub> and H<sub>2</sub>.

The outlet hydrogen molar flow rate of syngas ( $F_{\text{out,H}_2,\text{cir}}$ ) by using the circulation (cir = Y), or without (cir = N), can be assessed with the input and reacted hydrogen amounts ( $F_{\text{in,H}_2}$ ,  $F_{\text{re,H}_2,\text{cir}}$ ). The reacted hydrogen amount can be calculated by using Equations 7–8 and considering the molecules of H<sub>2</sub> ( $M_{\text{H}_2,\text{Re1}} = 1$  and  $M_{\text{H}_2,\text{Re2}} = 2$ ) during the Re1 and Re2 reactions.

$$F_{\text{out,H}_2,\text{cir}} = F_{\text{in,H}_2} + F_{\text{re,H}_2,\text{cir}} \quad \text{cir} = \text{N,Y} \quad (7)$$

$$F_{\text{re,H}_2,\text{cir}} = M_{\text{H}_2,\text{Re1}} \cdot (F_{\text{out,CO}} + F_{\text{out,CO,cir}}) + M_{\text{H}_2,\text{Re2}} \cdot (F_{\text{out,CO}_2} + F_{\text{out,CO}_2,\text{cir}}) \quad \text{cir} = \text{N,Y} \quad (8)$$

The outlet water molar flow rate of syngas ( $F_{\text{out,H}_2\text{O},\text{cir}}$ ) can be predicted with the input and reacted water amounts by using circulation (cir = Y) or without (cir = N), ( $F_{\text{in,H}_2\text{O}}$ ,  $F_{\text{re,H}_2\text{O},\text{cir}}$ ; Eq 9). The reacted water amount can be calculated with Equations 9–10, and the molecules of H<sub>2</sub>O ( $M_{\text{H}_2\text{O},\text{Re1}} = 1$  and  $M_{\text{H}_2\text{O},\text{Re2}} = 2$ ) of reactions Re1 and Re2.

$$F_{\text{out,H}_2\text{O},\text{cir}} = F_{\text{in,H}_2\text{O}} - F_{\text{re,H}_2\text{O},\text{cir}} \quad \text{cir} = \text{N,Y} \quad (9)$$

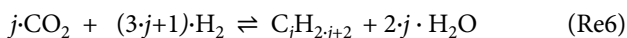
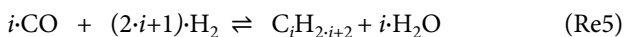
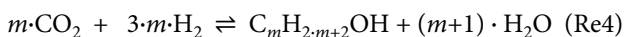
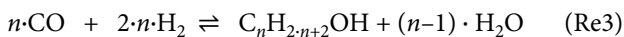
$$F_{\text{re,H}_2\text{O},\text{cir}} = M_{\text{H}_2\text{O},\text{Re1}} \cdot (F_{\text{out,CO}} + F_{\text{out,CO,cir}}) + M_{\text{H}_2\text{O},\text{Re2}} \cdot (F_{\text{out,CO}_2} + F_{\text{out,CO}_2,\text{cir}}) \quad \text{cir} = \text{N,Y} \quad (10)$$

The endothermic heat flow rate of syngas production ( $\phi_{\text{sgp,cir}}$ ; Eq 11) is dependent on the output carbon monoxide molar flow rate ( $F_{\text{out,CO}}$ ,  $F_{\text{out,CO,cir}}$ ) and the constant energy's parameter ( $a_{\text{sgp,cir}}$  into J/mol) by using circulation (cir = Y), or without (cir = N).

$$\phi_{\text{sgp,cir}} = (F_{\text{out,CO}} + F_{\text{out,CO,cir}}) \cdot a_{\text{sgp,cir}} \quad \text{cir} = \text{N,Y} \quad (11)$$

## 2. 2. The third part – The mathematical model of the different fuels' production

The third, or reaction part, for the different amounts of products' production ( $F_{\text{pr}}$ ; pr = 1...Pr; Eq 12) can be modelled with the basic simplified equations, which are dependent on the constant products' conversions of CO and CO<sub>2</sub> ( $X_{\text{CO,pr}}$ ,  $X_{\text{CO}_2,\text{pr}}$ ) and the output syngas molar flow rates ( $F_{\text{out,CO}}$ ,  $F_{\text{out,CO}_2}$ ,  $F_{\text{out,CO,cir}}$ ,  $F_{\text{out,CO}_2,\text{cir}}$ ) during the simplified reactions for alcohols (Re3 with  $n$  carbon atom, Re4 with  $m$  carbon atom) and alkanes (Re5 with the  $i$  carbon atom, Re6 with the  $j$  carbon atom), including molecules of CO and CO<sub>2</sub> ( $M_{\text{CO,pr}}$ ,  $M_{\text{CO}_2,\text{pr}}$ ) by using circulation (cir = Y), or without (cir = N).



$$F_{\text{pr,cir}} = X_{\text{pr,CO}} \cdot (F_{\text{out,CO}} + F_{\text{out,CO,cir}}) / M_{\text{CO,pr}} + X_{\text{pr,CO}_2} \cdot (F_{\text{out,CO}_2} + F_{\text{out,CO}_2,\text{cir}}) / M_{\text{CO}_2,\text{pr}} \quad \text{pr} = 1 \dots \text{Pr} \quad \text{cir} = \text{N,Y} \quad (12)$$

After the different products' production a lot of unreacted hydrogens remain, such as a coproduct for selling, which can be determined with Equation 13.

$$F_{\text{H}_2,\text{pr,cir}} = F_{\text{out,H}_2,\text{cir}} - [X_{\text{CO,pr}} \cdot (F_{\text{out,CO}} + F_{\text{out,CO,cir}}) \cdot M_{\text{H}_2,\text{CO,pr}} / M_{\text{CO,pr}} + X_{\text{CO}_2,\text{pr}} \cdot (F_{\text{out,CO}_2} + F_{\text{out,CO}_2,\text{cir}}) \cdot M_{\text{H}_2,\text{CO}_2,\text{pr}} / M_{\text{CO}_2,\text{pr}}] \quad \text{pr} = 1 \dots \text{Pr} \quad \text{cir} = \text{N,Y} \quad (13)$$

The released heat flow rates of the different products' production ( $\phi_{\text{pr,cir}}$ ; Eq 14) are dependent on the reacted products molar flow rates ( $F_{\text{pr,cir}}$ ) and the constant energy parameters ( $a_{\text{pr,cir}}$  into J/mol) by using circulation (cir = Y), or without (cir = N).

$$\phi_{\text{pr,cir}} = F_{\text{pr,cir}} \cdot a_{\text{pr,cir}} \quad \text{pr} = 1 \dots \text{Pr} \quad \text{cir} = \text{N,Y} \quad (14)$$

The fourth part for the different products' production contains the purification of individual products by using flashes and columns, where about 7 percent of the products and by-products are lost.

### 2. 3. The sixth part – The mathematical model of the fuels' blend

The individual synthetic fuels with different addition amounts can also be used as a new fuel mixture with new properties. Each additional component has the effects of boiling point, octane number, energy value, NO<sub>x</sub> particles, etc. The boiling point of the mixture ( $T_{bp,m}$ , Eq 15) is calculated by using the boiling point of the individual additional fuels ( $T_{bp,pr}$ ) and ratios ( $r_{pr}$ ).

$$T_{bp,m} = \sum r_{pr} \cdot T_{bp,pr} \quad pr = 1 \dots Pr \quad (15)$$

The molar flow rates of the fuel's mixture ( $F_{m,cir}$ , Eq 16) are determined by using the molar flow of the individual additional fuels ( $F_{pr,cir}$ ) and their ratios ( $r_{pr}$ ) by using circulation (cir = Y), or without (cir = N).

$$F_{m,cir} = \sum r_{pr} \cdot F_{pr,cir} \quad pr = 1 \dots Pr \quad cir = N, Y \quad (16)$$

The released heat flow rates of the fuel's mixture ( $\Phi_{m,cir}$ , Eq 17) are determined by using the released heat flow of the individual additional fuels ( $\Phi_{pr,cir}$ ) and their ratios ( $r_{pr}$ ) by using circulation (cir = Y), or without (cir = N).

$$\Phi_{m,cir} = \sum r_{pr} \cdot \Phi_{pr,cir} \quad pr = 1 \dots Pr \quad cir = N, Y \quad (17)$$

**Table 1:** Constant parameters' data with and without circulation.

| Constans by using circulation        | Constans without circulation     |
|--------------------------------------|----------------------------------|
| <b>1.Part</b>                        | <b>1.Part</b>                    |
| $X_{CO} = 0.969$                     | $X_{CO} = 0.969$                 |
| $X_{CO_2} = 0.031$                   | $X_{CO_2} = 0.031$               |
| $X_{CO,cir} = 0.7$                   | /                                |
| $a_{sgp,cir} = 31.5 \text{ kJ/mol}$  | $a_{sgp} = 33.4 \text{ kJ/mol}$  |
| <b>3.Part</b>                        | <b>3.Part</b>                    |
| <i>Methanol</i>                      | <i>Methanol</i>                  |
| $X_{CO,Me} = 0.65$                   | $X_{CO,Me} = 0.65$               |
| $a_{Me,cir} = -23.2 \text{ kJ/mol}$  | $a_{Me} = -24.3 \text{ kJ/mol}$  |
| <i>Ethanol</i>                       | <i>Ethanol</i>                   |
| $X_{CO,Et} = 1$                      | $X_{CO,Et} = 1$                  |
| $X_{CO_2,Et} = 0.9$                  | $X_{CO_2,Et} = 0.9$              |
| $a_{Et,cir} = -61.9 \text{ kJ/mol}$  | $a_{Et} = -62.4 \text{ kJ/mol}$  |
| <i>Synthetic gasoline</i>            | <i>Synthetic gasoline</i>        |
| $X_{CO,SG} = 1$                      | $X_{CO,SG} = 1$                  |
| $X_{CO_2,SG} = 0.9$                  | $X_{CO_2,SG} = 0.9$              |
| $a_{Me,cir} = -311.1 \text{ kJ/mol}$ | $a_{Me} = -316.3 \text{ kJ/mol}$ |

This presented carbon effect technique can analyse the predetermined amounts of multi alternative synthetic fuel products production from waste and flue gas quickly by using the carbon conversion into CO and CO<sub>2</sub>.

## 3. Case study of the carbon effect technique

The carbon effect technique was tested on the processing of methanol, ethanol and synthetic gasoline products. The technique was performed with and without circulation; the first was presented in more detail because of the usage of CO<sub>2</sub> emission, but the result of without circulation was included too. The tested individual synthetic fuels' productions produced methanol, ethanol and synthetic gasoline by using the same raw materials, such as sorted MSW with CO<sub>2</sub> emission circulation of the flue gas from the combustion unit.

### 3. 1. Case study – Methanol, ethanol and synthetic gasoline production

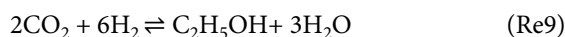
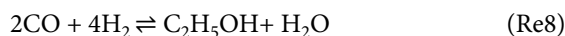
The methanol (pr = Me) was reacted by the catalytic hydrogenation of carbon monoxide only at 250 °C and 50 bar:



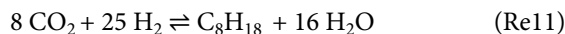
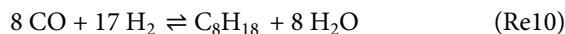
The ethanol (pr = Et) was synthesised by using the catalytic hydrogenation of carbon monoxide and dioxide at 250 °C and 50 bar:

**Table 2:** Results' data by using with and without circulation.

| Results by using circulation           | Results without circulation        |
|----------------------------------------|------------------------------------|
| <b>1.Part</b>                          | <b>1.Part</b>                      |
| $F_{out,CO} = 775 \text{ kmol/h}$      | $F_{out,CO} = 775 \text{ kmol/h}$  |
| $F_{out,CO_2} = 25 \text{ kmol/h}$     | $F_{out,CO_2} = 25 \text{ kmol/h}$ |
| $F_{out,CO,cir} = 105 \text{ kmol/h}$  | /                                  |
| $F_{out,CO_2,cir} = 45 \text{ kmol/h}$ | /                                  |
| $\phi_{sgp,cir} = 7.7 \text{ MW}$      | $\phi_{sgp} = 7.2 \text{ MW}$      |
| <b>3.Part</b>                          | <b>3.Part</b>                      |
| <i>Methanol</i>                        | <i>Methanol</i>                    |
| $F_{Me,cir} = 572 \text{ kmol/h}$      | $F_{Me} = 503 \text{ kmol/h}$      |
| $F_{H_2,Me,cir} = 1676 \text{ kmol/h}$ | $F_{H_2,Me} = 1617 \text{ kmol/h}$ |
| $\Phi_{Me,cir} = -3.7 \text{ MW}$      | $\Phi_{Me} = -3.4 \text{ MW}$      |
| <i>Ethanol</i>                         | <i>Ethanol</i>                     |
| $F_{Et,cir} = 471 \text{ kmol/h}$      | $F_{Et} = 398 \text{ kmol/h}$      |
| $F_{H_2,Et,cir} = 871 \text{ kmol/h}$  | $F_{H_2,Et} = 1007 \text{ kmol/h}$ |
| $\Phi_{Et,cir} = -8.1 \text{ MW}$      | $\Phi_{Et} = -6.9 \text{ MW}$      |
| <i>Synthetic gasoline</i>              | <i>Synthetic gasoline</i>          |
| $F_{SG,cir} = 118 \text{ kmol/h}$      | $F_{SG} = 99 \text{ kmol/h}$       |
| $F_{H_2,SG,cir} = 773 \text{ kmol/h}$  | $F_{H_2,SG} = 907 \text{ kmol/h}$  |
| $\Phi_{SG,cir} = -10.2 \text{ MW}$     | $\Phi_{SG} = -8.7 \text{ MW}$      |



Synthetic gasoline (pr = SG) was produced by the reaction of the carbon monoxide and at 250 °C and 20 bar:



The tested mathematical model included the real and simulated data, using the Aspen Plus<sup>®</sup> simulator for synthetic fuels products, such as methanol, ethanol and syngas (pr = Me, Et, SG). All the constant parameters' data for different fuels' production were included in Table 1, and all the results in Table 2 by using the circulated and uncirculated CO<sub>2</sub> emission. The tested input raw material, such as sorted municipal solid waste (MSW), were represented by the carbon and hydrogen molar flow rates ( $F_{\text{in,C}} = 800$  kmol/h;  $F_{\text{in,H}_2} = 1800$  kmol/h;), the circulated purified CO<sub>2</sub> emission ( $F_{\text{in,cir}} = 150$  kmol/h), and steam ( $F_{\text{in,H}_2\text{O}} = 1050$  kmol/h).

### 3. 2. Case study – The mathematical model of the syngas production

The Equations 1–10 of the first part enabled the calculation of the output molar flow rates of syngas, such as CO, CO<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>O, by using the CO<sub>2</sub> circulation ( $F_{\text{out,CO}}$ ,  $F_{\text{out,CO}_2}$ ,  $F_{\text{out,CO,cir}}$ ,  $F_{\text{out,CO}_2,\text{cir}}$ ,  $F_{\text{out,H}_2,\text{cir}}$ ,  $F_{\text{out,H}_2\text{O,cir}}$ ), and constant conversions of CO and CO<sub>2</sub> ( $X_{\text{CO}} = 0.969$ ,  $X_{\text{CO}_2} = 0.031$ ,  $X_{\text{CO,cir}} = 0.7$ ). The amounts of CO and CO<sub>2</sub>, which were obtained from the MSW carbon ( $F_{\text{out,CO}} = 775$  kmol/h,  $F_{\text{out,CO}_2} = 25$  kmol/h; Eqs 18–19) were enlarged because of the CO<sub>2</sub> emission with additional amounts ( $F_{\text{out,CO,cir}} = 105$  kmol/h,  $F_{\text{out,CO}_2,\text{cir}} = 45$  kmol/h; Eqs 20–21).

$$F_{\text{out,CO}} = X_{\text{CO}} \cdot F_{\text{in,C}} = 0.969 \cdot 800 = 775 \text{ kmol/h} \quad (18)$$

$$F_{\text{out,CO}_2} = X_{\text{CO}_2} \cdot F_{\text{in,C}} = 0.031 \cdot 800 = 25 \text{ kmol/h} \quad (19)$$

$$F_{\text{out,CO,cir}} = X_{\text{CO,cir}} \cdot F_{\text{in,cir}} = 0.7 \cdot 150 = 105 \text{ kmol/h} \quad (20)$$

$$F_{\text{out,CO}_2,\text{cir}} = F_{\text{in,cir}} - F_{\text{out,CO,cir}} = 150 - 105 = 45 \text{ kmol/h} \quad (21)$$

The outlet amounts of H<sub>2</sub> and H<sub>2</sub>O ( $F_{\text{out,H}_2,\text{cir}} = 2820$  kmol/h,  $F_{\text{out,H}_2\text{O,cir}} = 30$  kmol/h; Eqs 22–25) were determined by using circulation and Equations 7–10.

$$F_{\text{re,H}_2,\text{cir}} = M_{\text{H}_2,\text{Re1}} \cdot (F_{\text{out,CO}} + F_{\text{out,CO,cir}}) + M_{\text{H}_2,\text{Re2}} \cdot (F_{\text{out,CO}_2} + F_{\text{out,CO}_2,\text{cir}}) = 1 \cdot (775 + 105) + 2 \cdot (25 + 45) = 1020 \text{ kmol/h} \quad (22)$$

$$F_{\text{out,H}_2,\text{cir}} = F_{\text{in,H}_2} + F_{\text{re,H}_2,\text{cir}} = 1800 + 1020 = 2820 \text{ kmol/h} \quad (23)$$

$$F_{\text{re,H}_2\text{O,cir}} = M_{\text{H}_2\text{O,Re1}} \cdot (F_{\text{out,CO}} + F_{\text{out,CO,cir}}) + M_{\text{H}_2\text{O,Re2}} \cdot (F_{\text{out,CO}_2} + F_{\text{out,CO}_2,\text{cir}}) = 1 \cdot (775 + 105) + 2 \cdot (25 + 45) = 1020 \text{ kmol/h} \quad (24)$$

$$F_{\text{out,H}_2\text{O,cir}} = F_{\text{in,H}_2\text{O}} - F_{\text{re,H}_2\text{O,cir}} = 1050 - 1020 = 30 \text{ kmol/h} \quad (25)$$

The endothermic heat flow rate of the syngas production ( $\phi_{\text{sgp,cir}} = 7.7$  MW; Eq 26) was calculated by using Equation 11 and the constant energy's parameter ( $a_{\text{sgp,cir}} = 31.5$  kJ/mol).

$$\phi_{\text{sgp,cir}} = (F_{\text{out,CO}} + F_{\text{out,CO,cir}}) \cdot a_{\text{sgp,cir}} = (775 + 105) \cdot 31.5 = 7.7 \text{ MW} \quad (26)$$

After syngas production the condensate was removed and the syngas was compressed by the required pressure.

### 3. 3. Case study – The mathematical model of the different fuels' production

The third, or reaction part for the different amounts of the products' production ( $F_{\text{pr}}$ ; pr = Me, Et and SG; Eqs 27–29), were modelled with the basic simplified equations, which were dependent on the constant CO and CO<sub>2</sub> conversions ( $X_{\text{CO,Me}} = 0.65$ ,  $X_{\text{CO,Et}} = 1$ ,  $X_{\text{CO}_2,\text{Et}} = 0.9$ ,  $X_{\text{CO,SG}} = 1$ ,  $X_{\text{CO}_2,\text{SG}} = 0.9$ ), by using Equation 12 and reactions Re7–11.

$$F_{\text{Me,cir}} = X_{\text{Me,CO}} \cdot (F_{\text{out,CO}} + F_{\text{out,CO,cir}}) / M_{\text{CO,Me}} = 0.65 \cdot (770 + 105) / 1 = 572 \text{ kmol/h} \quad (27)$$

$$F_{\text{Et,cir}} = X_{\text{Et,CO}} \cdot (F_{\text{out,CO}} + F_{\text{out,CO,cir}}) / M_{\text{CO,Et}} + X_{\text{CO}_2,\text{Et}} \cdot (F_{\text{out,CO}_2} + F_{\text{out,CO}_2,\text{cir}}) / M_{\text{CO}_2,\text{Et}} = 1 \cdot (775 + 105) / 2 + 0.9 \cdot (25 + 45) / 2 = 471 \text{ kmol/h} \quad (28)$$

$$F_{\text{SG,cir}} = X_{\text{SG,CO}} \cdot (F_{\text{out,CO}} + F_{\text{out,CO,cir}}) / M_{\text{CO,SG}} + X_{\text{CO}_2,\text{SG}} \cdot (F_{\text{out,CO}_2} + F_{\text{out,CO}_2,\text{cir}}) / M_{\text{CO}_2,\text{SG}} = 1 \cdot (775 + 105) / 8 + 0.9 \cdot (25 + 45) / 8 = 118 \text{ kmol/h} \quad (29)$$

After the different products' production a lot of unreacted hydrogen remained, and the amounts were determined by using Equation 13 (Eqs 30–32).

$$F_{\text{H}_2,\text{Me,cir}} = F_{\text{out,H}_2,\text{cir}} - [X_{\text{CO,Me}} \cdot (F_{\text{out,CO}} + F_{\text{out,CO,cir}}) \cdot M_{\text{H}_2,\text{CO,Me}} / M_{\text{CO,Me}}] = 2820 - [0.65 \cdot (775 + 105) \cdot 2 / 1] = 1676 \text{ kmol/h} \quad (30)$$

$$F_{\text{H}_2,\text{Et,cir}} = F_{\text{out,H}_2,\text{cir}} - [X_{\text{CO,Et}} \cdot (F_{\text{out,CO}} + F_{\text{out,CO,cir}}) \cdot M_{\text{H}_2,\text{CO,Et}} / M_{\text{CO,Et}} + X_{\text{CO}_2,\text{Et}} \cdot (F_{\text{out,CO}_2} + F_{\text{out,CO}_2,\text{cir}}) \cdot M_{\text{H}_2,\text{CO}_2,\text{Et}} / M_{\text{CO}_2,\text{Et}}] = 2820 - [1 \cdot (775 + 105) \cdot 4 / 2 + 0.9 \cdot (25 + 45) \cdot 6 / 2] = 871 \text{ kmol/h} \quad (31)$$

$$F_{H_2,SG,cir} = F_{out,H_2,cir} - [X_{CO,SG} \cdot (F_{out,CO} + F_{out,CO,cir}) \cdot M_{H_2,CO,SG} / M_{CO,SG} + X_{CO_2,SG} \cdot (F_{out,CO_2} + F_{out,CO_2,cir}) \cdot M_{H_2,CO_2,SG} / M_{CO_2,SG}] = (32) \\ 2820 - [1 \cdot (775 + 105) \cdot 17/8 + 0.9 \cdot (25 + 45) \cdot 25/8] = 773 \text{ kmol/h}$$

The released heat flow rates of the different products' production were calculated by using Equation 14 and the constant energy' parameters ( $a_{Me,cir} = -23.2 \text{ kJ/mol}$ ,  $a_{Et,cir} = -61.9 \text{ kJ/mol}$ ,  $a_{Me,cir} = -311.1 \text{ kJ/mol}$ ; Eqs 33–35).

$$\Phi_{Me,cir} = F_{Me,cir} \cdot a_{Me,cir} = 572 \cdot 23.2 = -3.7 \text{ MW} \quad (33)$$

$$\Phi_{Et,cir} = F_{Et,cir} \cdot a_{Et,cir} = 471 \cdot 61.9 = -8.1 \text{ MW} \quad (34)$$

$$\Phi_{SG,cir} = F_{SG,cir} \cdot a_{SG,cir} = 118 \cdot 311.1 = -10.2 \text{ MW} \quad (35)$$

The fourth part of the flow-diagram for the different fuels' production contained the purification of individual products by using the same purification system units, where about 7 percent of the products and by-products were lost.

The all-important parameters were determined of the common synthesis gas and individual fuels with and without circulation (Table 2). The amount of CO, CO<sub>2</sub> and H<sub>2</sub> of synthesis gas were determined with a calculated value of 880, 70 and 2820 kmol/h, respectively, which were more than 13.5, 180 and 7% by using circulation of the CO<sub>2</sub> emission. The endothermic heat flow rate of the syngas production was 7.7 MW, which was higher by 7% by using circulation of the CO<sub>2</sub> emission. The different amounts of synthetic fuels, such as methanol, ethanol and gasoline, were produced with calculated values of 572, 471 and 118 kmol/h, respectively, which were more by 13.7, 18 and 19% by using circulation of the CO<sub>2</sub> emission. The released heat flow rates of different fuels, such as methanol, ethanol and gasoline were 3.7, 8.1 and 10.2 MW, respectively, which were more by 9, 17 and 17% by using circulation of the CO<sub>2</sub> emission.

There are many possible fuels' blending combinations, but the optimal blend was chosen, which contained 10% ethanol and 90% gasoline, because of the increased octane numbers. The molar flow rate (Eq 16) and released heat flow rate (Eq 17) of the optimal blend mixture were determined with the calculated value of 153 kmol/h and 10 MW with a boiling point of 121 °C (Eq 15) by using circulation.

## 4. Conclusions

We strive to minimise the usage of plastic, but it is not so easy to give it up, so we aim to recycle it, and old unusable plastic can be produced into individual or mixed fuels by using the carbon effect technique. This presented carbon effect technique bases on the inlet carbon amount

into raw materials, such as purified municipal solid waste and with or without circulation of the CO<sub>2</sub> emission from the flue gas, which can predetermine the amounts of common syngas production and different synthetic fuels quickly, including the energy consumption or production. The carbon conversions of CO and CO<sub>2</sub> were performed according to calculated constant values and energy' parameters by using real and simulated data with an Aspen Plus<sup>®</sup> simulator.

The carbon effect technique was tested on the multi alternative production of synthetic fuel productions, such as methanol, ethanol and gasoline, by using MSW and with circulation of the CO<sub>2</sub> emission from the flue gas, which can reduce CO<sub>2</sub> emissions by 3.5 10<sup>6</sup> kmol/a. The highest amounts of methanol, ethanol and gasoline were produced with the calculated values of 572, 471 and 118 kmol/h, respectively, by using circulation of the CO<sub>2</sub> emissions. The individually synthetic fuels had increased productions between 14 and 19% because of the CO<sub>2</sub> circulation considerations. The energy consumptions or productions were enlarged between 7 and 17% by using circulation of the CO<sub>2</sub> emissions. The more efficient blend fuel was the mixture of 10% ethanol and 90% gasoline, because the added ethanol increased the octane numbers of the fuel. During the fuels' production a lot of available hydrogen remained, with calculated values of 1676, 871 and 773 kmol/h, respectively, with CO<sub>2</sub> circulation.

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## Povzetek

Predstavljena je več-alternativna metoda Tehnika ogljikovega učinka, za proizvodnjo različnih sintetičnih goriv iz prečiščenih trdnih komunalnih odpadkov in CO<sub>2</sub> iz dimnega plina. Novost te študije je, da temelji na matematičnemu modelu z realnimi in deloma simuliranimi (Aspen Plus<sup>®</sup>) podatki. Ta metoda že v naprej določa predvidene proizvedene količine sintetičnih goriv in njihove glavne energetske porabe v odvisnosti od prisotne količine ogljika v surovini in nadaljnji presnovi ogljika v CO in CO<sub>2</sub>. Več-alternativno metodo smo testirali s proizvodnjo različnih sintetičnih goriv, kot so metanol, etanol in bencin. Posamezna proizvedena sintetična goriva se lahko uporabijo tudi kot nova mešanica goriv.



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