Converting Waste into Products and Energy Using Complete Circular Economy and the Hydrogen Effect Technique to Reduce Dependence on Natural Gas



A. Kovač Kralj^{*}

doi: https://doi.org/10.15255/CABEQ.2022.2157

Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova 17, Maribor, Slovenia

Original scientific paper Received: November 2, 2022 Accepted: May 18, 2023

Conversion of waste into products and energy has the potential to reduce CO_2 emission through implementation of a complete circular economy and utilisation of the hydrogen effect technique. This study considers the novelties of the hydrogen effect technique, which incorporates an upgraded input unit mathematical model. It includes real-simulated results obtained using an Aspen Plus[®] simulator, and enlarged production. This technique is developed for optimal municipal solid waste (MSW) combustion, gasification, and reforming, presented as an upgraded input unit for syngas production, which can reduce CO_2 emissions by $3 \cdot 10^6$ kmol a⁻¹. This approach is exemplified by utilizing existing methanol and dimethyl ether production processes from natural gas, as they can be achieved and exceeded using MSW with varying hydrogen amounts. The optimal upgraded methanol and dimethyl ether production processes can increase production by 47 % and 16 %, including only the upgraded input unit, as well as decrease the temperature in the product reactors by 30 °C.

Keywords

waste gasification, flue gas, syngas, hydrogen, circular economy, combustion

Introduction

The global quantity of municipal solid waste (MSW) being disposed of in landfills has been increasing significantly, imposing the need to use it as valuable raw material. Co-gasification of MSW, as a conversion technology has the potential to generate useful energy and sustainable co-products.

Lee et al. presented an analysis of waste gasification and its potential role in China's transition towards carbon neutrality and zero waste cities. The article presents opportunities for waste gasification to contribute to China's transition in these areas.¹ Hasanzadeh and co-workers researched 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 polyethylene waste gasification. The findings revealed that hydrogen production had improved significantly, by 48 %, by raising the steam to polyethylene waste ratio according to the water-gas shift and reforming reactions. The hydrogen production and exergy efficiencies were enhanced by increasing the temperature.²

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 a process based on two steps: Pyrolysis and in-line intensification for olefin production by means of catalytic cracking or thermal cracking at high temperatures.³

Messerle and researchers presented the thermodynamic analysis and experiments on gasification of biomedical waste in a plasma reactor. The calculations showed that the maximum yield of synthesis gas in the waste plasma gasification in air and steam medium was achieved at a temperature not higher than 1600 K.⁴

Beyene *et al.* presented the waste-to-energy (WtE) technologies, which advance toward using MSW to produce renewable energy. The article explains current and future WtE conversion technologies. In addition, the authors suggested future WtE trends, and directions for efficient methods of converting MSW for the generation of renewable ener-

^{*}Phone: +386 02 2294454, Fax: +386 02 2527 774; E-mail: anita.kovac@uni-mb.si

gy, with a focus on waste recovery. This review highlights recent and emerging WtE technologies, which are less published. Specifically, the production of hydrogen energy from municipal solid waste (MSW) is a new insight in the field of WtE conversion technology.⁵

Pan *et al.* presented a hybrid design that combines waste gasification and coal-fired power generation, 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 precooled by the feed water of the coal power plant, and then conveyed directly into the coal-fired boiler for combustion.⁶

Frolov *et al.* proposed to produce highly superheated steam (HSS) for environmentally friendly steam-assisted gasification of organic municipal and industrial wastes using cyclic detonations of ternary propane/methane–oxygen–steam mixtures.⁷

Lam *et al.* developed the two-stage optimisation model consisting of a 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. The macro-stage handles the synthesis and optimisation of the waste-to-energy supply network.⁸

Cucchiella *et al.* presented a strategic analysis of the quantities of waste required for incineration with energy recovery, considering different approaches based on unsorted waste, landfilled waste, and separated collection rates, respectively. Consequently, the sustainability of a WtE (Waste to Energy) plant is evaluated as an alternative to landfill for a specific area.⁹

Diyoke *et al.* developed a gasification model in Matlab to simulate a downdraft gasifier using wood as feedstock. The downdraft gasifier was divided conceptually into three zones: pyrolysis zone, combustion/oxidation zone, and reduction zone.¹⁰

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 determined that steam gasification was superior to the other options, due to its capacity and clean by-product gases.¹¹

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 CO₂ adsorbents.¹²

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.¹³

Barontini *et al.* presented the co-gasification of woody biomass with organic and waste matrices in a downdraft gasifier. The model was calibrated with the experimental data, and proved to fit the syngas composition and physical properties with satisfying accuracy.¹⁴

Chanthakett *et al.* conducted a critical assessment of waste-to-energy gasification technology for municipal solid waste, focusing on processing, energy recovery, environmental performance, and economic perspectives. The study also explored and identified suitable simulation tools for optimising gasification.¹⁵

Lee *et al.* studied compressed natural gas and ethanol production from MSW.¹⁶

Pyrolysis processes convert waste into biochar, bio-oil, and gases,¹⁷ and such bio-oil can be hydro-processed further to produce gasoline and diesel blend stocks.¹⁸

Fujii and co-workers presented a combined system, which would use biogas to heat steam recovered from an incineration boiler with separate superheating equipment.¹⁹

Soltanieh *et al.* studied the implementation of large-scale polygeneration plants, which use multiple feeds (such as coal and natural gas), and produce multiple products (such as power, liquid fuels and chemicals).²⁰

Puig-Gamero and co-workers used Aspen Plus® for modelling methanol synthesis from synthesis gas obtained through pine biomass gasification.²¹ Tungalag and researchers described the gasification of municipal solid waste for synthesis gas production, including a simulation using Aspen Plus[®].²² Their research was based on synthesis gas production using pyrolysis and plasma gasification, but not methanol production. 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.²³ Borgogna and researchers described methanol production from refuse-derived fuel, including the influence of feedstock composition on process yield through gasification analysis.²⁴

In this study, the waste raw material can be converted into syngas which can then be used for the production of sustainable liquid and gaseous products utilizing the hydrogen effect technique. This technique includes a complete circular economy into the upgraded input unit, including combustion, gasification, and reforming. Municipal solid waste with varying amounts of hydrogen could replace conventional natural gas, thereby reducing the dependence on natural gas. Additionally, introducing hydrogen into MSW has a significant effect on increasing production of valuable products.

Hydrogen effect technique

The reuse of waste has received considerable attention due to increasing waste generation worldwide. One of the solutions for waste disposal, which has been implemented widely, is co-gasification. Recycling can extract some useful materials from waste; however, not all waste can be recycled, which is then transferred to landfills as municipal solid waste (MSW). MSW includes sorted, non-recycled plastics and wood, mostly without rubber, leather, textiles, etc. The principal concept of waste gasification is conversion of waste into the production of liquid or/and gaseous chemicals and energy, thereby reducing the dependence on natural gas. This study presents the hydrogen effect technique, which is based on upgraded input unit for MSW processing, a mathematical model including real-simulated results using the Aspen Plus® simulator, and enlarged production. The existing reforming unit can be enlarged with combustion and gasification for MSW processing (Fig. 1). The upgraded input unit includes three parts: Combustion, gasification, and reforming with necessary added steam. The purified flue gas (without particles, NO₂, SO, oxygen, and nitrogen) from combustion, including steam and carbon dioxide, is transported circularly into the gasification-reforming part. This is the only input retrofit, while the other process units of the plant remain the same. The existing chemical processes, which use natural gas as raw material, can be replaced with MSW gasification into syngas production.

MSW (as components of C and H₂) and the purified circulated flue gas (as components of CO₂, H₂O) can enter as complete circular economy systems. Syngas (as components of CO, CO₂, H₂, H₂O, CH₄) are reacted using reaction 1 (Re1). The molar balance of elements (C, H and O), including the input (F_{in}) and output (F_{out}) molar flow rate, using reaction 1, are presented with Equations 1–3.

$$C + H_{2} + H_{2}O + CO_{2} \rightleftharpoons H_{2} + H_{2}O + CO_{2} + CO (Re1)$$
$$C: F_{in,C} + F_{in,CO_{2}} = F_{out,CO_{2}} + F_{out,CO}$$
(1)

H: 2
$$F_{in,H_2}$$
 + 2 F_{in,H_2O} = 2 F_{out,H_2} + 2 F_{out,H_2O} (2)

O:
$$F_{\text{in},\text{H}_2\text{O}} + 2F_{\text{in},\text{CO}_2} = F_{\text{out},\text{H}_2\text{O}} + 2F_{\text{out},\text{CO}_2} + F_{\text{out},\text{CO}}$$
 (3)

The quality of the MSW changes between minimum and maximum hydrogen amounts. MSW can contain 40 % plastics and 60 % wood; this is presented as the basic quality, with the minimum hydrogen molar flow rate $(F_{\rm H_2,min})$. The additional hydrogen flow rate $(\Delta F_{\rm H_2})$ can be increased by 30 %, which depends on a larger amount of plastic in the MSW:

$$\Delta F_{\rm H_2} = F_{\rm H_2,max} - F_{\rm H_2,min} = 30 \%$$
 (4)



Fig. 1 - Flow-diagram of the hydrogen effect technique

The hydrogen effect technique is presented with a mathematical model, depending on the real-simulated results using the Aspen Plus[®] simulator, which can easily determine the constant linear slopes (a) for the calculation of the required variables (as the heat flow rates and molar flow rates). All the necessary constants and minimum amounts can be obtained from the simulation.

The heat flow rate of the upgraded input unit $(\phi_{\text{in-ret}})$ is dependent on the additional hydrogen (ΔF_{H_2}) and the constant unit slope $(a_{\text{in-ret}})$:

$$\phi_{\text{in-ret}} = \phi_{\text{in-ret,min}} + a_{\text{in-ret}} \cdot \Delta F_{\text{H}_2}$$
(5)

The molar flow rate composition of the syngas from the upgraded input unit can be calculated using Equation 6. The syngas consists of components $(F_{sg,com})$ of H₂, H₂O, CO, CO₂, depending on the minimum molar flow rate $(F_{sg,com,min})$, the additional hydrogen (ΔF_{H_2}) , and the constant component effect slope $(a_{sg,com})$:

$$F_{\rm sg,com} = F_{\rm sg,com,min} + a_{\rm sg,com} \cdot \Delta F_{\rm H_2}$$

$$com = H_2, H_2O, CO, CO_2$$
(6)

The hydrogen effect technique includes only input upgraded unit, while other units remain the same because of the existing process flexibility. Non-retrofitted units are composed of cooling, condensation, and compressing the syngas. The production of products within the reactor can also be changed. The outlet stream of the reactor includes the components ($F_{\rm rg,com}$) of H₂, H₂O, CO, CO₂, and product (methanol; MeOH or dimethyl ether; DME), depending on the minimum molar flow rate ($F_{\rm rg,com,min}$), the additional hydrogen ($\Delta F_{\rm H_2}$), and the constant component effect slope ($a_{\rm rg,com}$):

$$F_{\rm rg,com} = F_{\rm rg,com,min} + a_{\rm rg,com} \cdot \Delta F_{\rm H_2}$$

com = H₂, H₂O, CO, CO₂, product (7)

The heat flow rate of reactor (ϕ_{re}) is dependent on the additional hydrogen and the constant unit slope (a_{re}) :

$$\phi_{\rm re} = \phi_{\rm re,min} + a_{\rm re} \cdot \Delta F_{\rm H_2} \tag{8}$$

The hydrogen effect technique can determine the important values from minimum to maximum of syngas and products productions, depending on a lower to higher hydrogen amount of MSW and the real-simulated results of the Aspen Plus[®] simulator.

Case study of the hydrogen effect technique for methanol production

The hydrogen effect technique was tested on the existing crude methanol process,^{25,26} replacing unsustainable natural gas with otherwise useless MSW (such as plastic and wood) and flue gas from combustion.

Simulation of existing methanol production from natural gas

The existing crude methanol process was well adapted using the Aspen Plus[®] simulator. The natural gas (almost 100 % methane; $F_{\rm CH_4} = 1240$ kmol h⁻¹) for syngas production was firstly desulphurised, and then heated within a steam reformer (Ref; using reactor Rgibbs from Aspen Plus[®]), where syngas was produced from the natural gas and steam ($F_{\rm H_{2}O} = 2000$ kmol h⁻¹) on NiO catalyst at 800 °C and 9 bar:

CH₄ + H₂O ≈ CO + 3H₂
$$\Delta_{\rm r}^{H^{298}}$$
 = 206.08 kJ mol⁻¹ (Re2)
CO + H₂O ≈ CO₂ + H₂ $\Delta_{\rm r}^{H^{298}}$ = -41.17 kJ mol⁻¹ (Re3)

The hot stream of syngas ($F_{\rm CO_2} = 223$ kmol h⁻¹, $F_{\rm CO} = 668$ kmol h⁻¹, $F_{\rm CH_4} = 348$ kmol h⁻¹, $F_{\rm H_2} = 2897$ kmol h⁻¹, $F_{\rm H_2O} = 885$ kmol h⁻¹) was cooled within many heat exchangers to 40 °C, water condensed and compressed to 50 bar. The reactor's inlet was heated to 225 °C. Methanol was produced by the catalytic hydrogenation of carbon monoxide and/or carbon dioxide within an exothermic reactor (R; using a Requil reactor from Aspen Plus[®]; $\phi_{\rm R} = 14$ MW ²⁶), using two main reactions at 250 °C:

$$CO + 2H_{2} \rightleftharpoons CH OH$$

$$\Delta_{r}H = -90.77 \text{ kJ mol}^{-1} \qquad \overset{3}{X}_{CO} = 65 \% \quad (\text{Re4})$$

$$CO_{2} + 3H_{2} \rightleftharpoons CH OH + H O$$

$$\Delta_{r}H = -49.58 \text{ kJ mol}^{-1} \qquad X_{CO_{2}} \stackrel{2}{=} 30 \% \quad (\text{Re5})$$

The reactor's outlet was cooled to 40 °C. The separator for the product and unreacted gas separation was separated into 540 kmol h⁻¹ crude methanol ($F_{CH_{3}OH,ex}$) at 40 °C and 40 bar. The crude methanol was cleaned within the distillation columns (this part of the process was not included in this research).

Hydrogen effect technique for methanol production

Conventional natural gas could be replaced with MSW (including plastic and wood) as raw materials using the same simulated model and parameters (Section Simulation of existing methanol production from natural gas), and only changing the raw material and input unit. The existing reforming unit can be enlarged with combustion and gasification using the upgraded input unit. The other process units of the plant remained the same (Section Simulation of existing methanol production from natural gas). The MSW was presented as composed from C and H₂. The MSW was combusted, gasified, and reformed into the upgraded input unit (Fig. 2). The purified flue gas of combustion, including steam and carbon dioxide, was transported into the upgraded input unit, where the syngas was generated (CO, CO_2 , H_2) using reaction Re1.



Fig. 2 – Flow-diagram of the hydrogen effect technique for the case study

The MSW contained 40 % plastics and 60 % wood (800 kmol h⁻¹ of C and 1500 kmol h⁻¹ of H₂), which was presented as a minimum hydrogen composition ($F_{\rm H_2,min}$). The amount of hydrogen in MSW can be increased by 30 %. MSW which contained 60 % plastics and 40 % wood ($F_{\rm H_2,max}$: 800 kmol h⁻¹ of C and 2000 kmol h⁻¹ of H₂), was presented as maximum hydrogen composition ($F_{\rm H_2,max}$). The purified flue gas (without particles, NO_x, SO_x and nitrogen; $F_{\rm CO_2,in} = 240$ kmol h⁻¹; $F_{\rm H_2O,in} = 920$ kmol h⁻¹) flowed into the upgraded input unit.

The higher heat flow rate into the upgraded input unit ($\phi_{\text{in-ret}} = 26.1 \text{ MW}$) was dependent on the additional hydrogen ($\Delta F_{\text{H}_2} = 0-500$ in kmol h⁻¹), and the constant unit slope ($a_{\text{in-ret}} = 0.0003$ MW kmol⁻¹ h⁻¹), obtained with the real-simulated results using the Aspen Plus[®] simulator. The maximum heat flow rate into the upgraded input unit was 26.25 MW using the maximum additional hydrogen:

$$\phi_{\text{in-ret}} = \phi_{\text{in-ret,min}} + a_{\text{in-ret}} \cdot \Delta F_{\text{H}_2} = 26.25 \text{ MW} \quad (9)$$

The higher molar flow rate composition of the syngas after the upgraded input unit was calculated using Equation 6. The syngas ($F_{sg,com}$), including H₂, H₂O, CO, CO₂, was determined with the minimum flow rate ($F_{sg,com,min}$ in kmol h⁻¹), the additional hydrogen ($\Delta F_{H_2} = 0-500$), and the constant component effect slope ($a_{sg,com}$). The higher molar flow rates of syngas were:

$$F_{\rm sg,H_2} = F_{\rm sg,H_2,min} + a_{\rm sg,H_2} \cdot \Delta F_{\rm H_2} = 2174 + 0.97 \cdot \Delta F_{\rm H_2} = 2660 \text{ kmol } h^{-1}$$
(10)

$$F_{\rm sg,H_2O} = F_{\rm sg,H_2O,min} + a_{\rm sg,H_2O} \cdot \Delta F_{\rm H_2} = 245 + 0.03 \cdot \Delta F_{\rm H_2} = 260 \text{ kmol } h^{-1}$$
(11)

$$F_{sg,CO} = F_{sg,CO,min} + a_{sg,CO} \cdot \Delta F_{H_2} = 925 + 0.03 \cdot \Delta F_{H_2} = 940 \text{ kmol } h^{-1}$$
(12)

$$F_{\rm sg,CO_2} = F_{\rm sg,CO_2,min} + a_{\rm sg,CO_2} \cdot \Delta F_{\rm H_2} = 114 - 0.03 \cdot \Delta F_{\rm H_2} = 100 \text{ kmol } h^{-1}$$
(13)

The additional outlet molar flow rate ratio between H_2 and other components was always the same, as follows:

$$\Delta F_{\rm H_2}:\Delta F_{\rm sg.com} = 0.97:0.03$$
 (14)

The hydrogen effect technique was upgraded, while the other units remain the same because of the existing process flexibility. Non-retrofitted units were composed of cooling, condensation, and compressing syngas, as in Section Simulation of existing methanol production from natural gas. The methanol production in the reactor can be raised, depending on the additional hydrogen, using reactions Re4 and Re5. The outlet stream of the reactor consisted of components ($F_{\rm rg,com}$) of H₂, H₂O, CO, CO₂ and methanol (MeOH; Eq.7), which were dependent on the minimum molar flow rate ($F_{\rm rg,com}$, he additional hydrogen ($\Delta F_{\rm H_2}$), and the constant

component effect slope (a_{rg,com}) at 250 °C. The higher molar flow rates with $\Delta F_{\rm H_2} = 500$ kmol h⁻¹ in the methanol reactor were:

$$F_{\rm rg,MeOH} = F_{\rm rg, MeOH,min} + a_{\rm rg, MeOH} \cdot \Delta F_{\rm H_2}$$

= 559 + 0.113 \cdot \Delta F_{\rm H_2} = 616 \kmol h^{-1} (15)

$$F_{\rm rg,H_2} = F_{\rm rg,H_2,min} + a_{\rm rg,H_2} \cdot \Delta F_{\rm H_2}$$

= 1087 + 0.743 \cdot \Delta F_{\rm H_2} = 1461 \kmol \kmol \kmol \kmol \Lambda^{-1} (16)

$$F_{\rm rg,H_2O} = F_{\rm rg,H_2O,min} + a_{\rm rg,H_2O} \cdot \Delta F_{\rm H_2} = 6 + 0.004 \cdot \Delta F_{\rm H_2} = 8 \text{ kmol } h^{-1}$$
(17)

$$F_{\rm rg,CO} = F_{\rm rg,CO,min} + a_{\rm rg,CO} \cdot \Delta F_{\rm H_2}$$

= 335 -0.094 \cdot \Delta F_{\rm H_2} = 288 \kmol h^{-1} (18)

$$F_{\rm rg,CO_2} = F_{\rm rg,CO_2,min} + a_{\rm rg,CO_2} \cdot \Delta F_{\rm H_2} = 145 - 0.022 \cdot \Delta F_{\rm H_2} = 134 \text{ kmol } h^{-1}$$
(19)

The methanol product was dependent on the temperature effect in the reactor (Fig. 3). The lower temperature drop by 30 °C of the existing temperature (250 °C, $\Delta T_{\rm re} = 30$ °C) can raise the methanol production in Re4, depending on the constant temperature slope (a_{rg,tem} = 6). The optimal methanol production was:

$$F_{\rm rg,MeOH,op} = F_{\rm rg,MeOH} + a_{\rm rg,tem} \cdot \Delta T_{\rm re} = 616 + 6 \cdot 30$$

= 796 kmol h⁻¹ (20)

Reaction Re4 had the most effect on temperature, which raised methanol production by 180 kmol h^{-1} , and then decreased the CO by the same amount, and H₂ by twice that value in the outlet stream:

$$F_{\rm rg,CO,op} = F_{\rm rg,CO} + a_{\rm rg,tem} \cdot \Delta T_{\rm re} = 288 - 6 \cdot 30$$

= 108 kmol h⁻¹ (21)

$$F_{\rm rg,H_2,op} = F_{\rm rg,H_2} + a_{\rm rg,tem} \cdot \Delta T_{\rm re} = 1461 - 2 \cdot 6 \cdot 30 = 1100 \text{ kmol } h^{-1}$$
(22)



Fig. 3 – Using the additional hydrogen and temperature effect of methanol production

Using the waste with the lower hydrogen amount, the minimum methanol ($F_{\rm rg,MeOH,min}$) of 559 kmol h⁻¹ can be produced, which can be compared to the conventional methanol production ($F_{\rm CH_3OH,ex} = 540$ kmol h⁻¹) from natural gas. Using the additional hydrogen and temperature effect can produce the optimal methanol molar flow rate ($F_{\rm rg,MeOH,op}$) of 796 kmol h⁻¹, and the methanol production can be increased by 47 % with regard to conventional production ($F_{\rm CH_3OH,ex} = 540$ kmol h⁻¹) from natural gas. This modification was included only in the input unit, with decreased temperature in the methanol reactor by 30 °C.

The higher exothermal heat flow rate of the methanol reactor was dependent on the minimum heat flow rate (-15.7 MW), additional hydrogen ($\Delta F_{\rm H,}$ = 500 kmol h⁻¹), the constant unit slope (a_{re} =0.0024 MW kmol⁻¹ h⁻¹), and the drop in temperature effect (a_{re,tem} = 0.16, by ΔT = 30 °C):

$$\phi_{\rm re} = \phi_{\rm re,min} + a_{\rm re} \cdot \Delta F_{\rm H_2} + a_{\rm re,tem} \cdot \Delta T = -22.1 \text{ MW } (23)$$

The exothermal heat flow rate of the methanol reactor can increase the steam production by 50 %, compared to the conventional production from natural gas.

Hydrogen effect technique for dimethyl ether production

The syngas production was the same as in Section Hydrogen effect technique for methanol production, only the reactor was different. The dimethyl ether production in the reactor can be raised depending on the additional hydrogen using reaction Re6.

$$2 \text{ CO/CO}_2 + 6 \text{ H}_2 \rightleftharpoons \text{CH}_3\text{OCH}_3 + 3 \text{ H}_2\text{O} \text{ (Re6)}$$

The outlet stream of the reactor included components ($F_{\rm rgDE,com}$) of H₂, H₂O, CO, CO₂ and dimethyl ether (DME; Eq. 7), which were dependent on the minimum molar flow rate ($F_{\rm rgDE,com,min}$), the additional hydrogen ($\Delta F_{\rm H_2}$), and the constant component effect slope ($a_{\rm rgDE,com}$) at 250 °C. The higher molar flow rates with $\Delta F_{\rm H_2}$ = 500 kmol h⁻¹ in DME reactor were:

$$F_{\rm rgDE,DME} = F_{\rm rgDE,DME,min} + a_{\rm rgDE,DME} \cdot \Delta F_{\rm H_2}$$

= 289 + 0.034 \cdot \Delta F_{\rm H_2} = 306 kmol h^{-1} (24)

$$F_{\rm rgDE,H_2} = F_{\rm rgDE,H_2,min} + a_{\rm rgDE,H_2} \cdot \Delta F_{\rm H_2} = 1331 + 0.80 \cdot \Delta F_{\rm H_2} = 1730 \text{ kmol } h^{-1}$$
(25)

$$F_{\rm rgDE,H_{2}O} = F_{\rm rgDE,H_{2}O,min} + a_{\rm rgDE,H_{2}O} \cdot \Delta F_{\rm H_{2}} = 219 + 0.1 \cdot \Delta F_{\rm H_{2}} = 270 \text{ kmol } h^{-1}$$
(26)

$$F_{\rm rgDE,CO} = F_{\rm rgDE,CO,min} + a_{\rm rgDE,CO} \cdot \Delta F_{\rm H_2} = 31 - 0.002 \cdot \Delta F_{\rm H_2} = 30 \text{ kmol } h^{-1}$$
(27)

$$F_{\rm rgDE,CO_2} = F_{\rm rgDE,CO_2,min} + a_{\rm rgDE,CO_2} \cdot \Delta F_{\rm H_2} = 430 - 0.07 \cdot \Delta F_{\rm H_2} = 395 \text{ kmol } \text{h}^{-1}$$
(28)



Fig. 4 – Using the additional hydrogen and temperature effect of DME production

The DME product was dependent on the temperature effect in the reactor (Fig. 4). The lower temperature drop by 30 °C from the existing temperature (250 °C, $\Delta T_{\text{reDE}} = 30$ °C) can raise the DME production, depending on the constant temperature slope (a_{rgDE,tem} = 1.4). The optimal DME production was:

$$F_{\rm rgDE,DME,op} = F_{\rm rgDE,DME} + a_{\rm rgDE,tem} \cdot \Delta T_{\rm reDE}$$

= 306 + 1.4 \cdot 30 = 348 kmol h⁻¹ (29)

CO conversion into DME had the greatest temperature effect, which raised DME production, thus decreasing the CO and H_2 amounts in the outlet stream:

$$F_{\rm rgDE,CO,op} = F_{\rm rgDE,CO} + a_{\rm rgDE,tem} \cdot \Delta T_{\rm reDE}$$

= 30 -2 \cdot 1.4 \cdot 30 = 9 kmol h⁻¹ (30)

$$F_{\rm rgDE,H_2,op} = F_{\rm rgDE,H_2} + a_{\rm rgDE,tem} \cdot \Delta T_{\rm reDE} = 1730 - 6 \cdot 1.4 \cdot 30 = 1478 \text{ kmol } \text{h}^{-1}$$
(31)

The minimum amount of DME that can be produced using waste with the lower hydrogen amount $(F_{rgDE,DME,min})$ is 306 kmol h⁻¹, which approaches the conventional DME production $(F_{DME,ex} = 300$ kmol h⁻¹) from natural gas. Using the additional hydrogen and temperature effect can produce the optimal DME molar flow rate $(F_{rgDE,DME,op})$ of 348 kmol h⁻¹, and the DME production can be increased by 16 %, with regard to the conventional production from natural gas. This modification included only the input unit upgrade, and decreased temperature in the DME reactor by 30 °C. The higher exothermal heat flow rate of the DME reactor was dependent on the minimum heat flow rate (-21.1 MW), additional hydrogen ($\Delta F_{\rm H_2}$ = 500 kmol h⁻¹), the constant unit slope ($a_{\rm reDE} = 0.0016$ MW kmol⁻¹ h⁻¹), and the drop temperature effect ($a_{\rm reDE,tem} = 0.06$, by $\Delta T = 30$ °C):

$$\phi_{\text{reDE}} = \phi_{\text{reDE,min}} + a_{\text{reDE}} \cdot \Delta F_{\text{H}_2} + a_{\text{reDE,tem}} \cdot \Delta T = -23.7 \text{ MW} (32)$$

The exothermal heat flow rate of the DME reactor can increase steam production by 17 %, with regard to conventional production from natural gas.

Conclusions

In many countries, natural gas can be replaced with MSW, which, as useless waste can be converted into liquid and gaseous products (such as methanol and DME), while the accumulation of the waste on the landfill can be reduced using the hydrogen effect technique. This technique includes the upgraded input unit mathematical model depending on the real-simulated results of the Aspen Plus® simulator and hydrogen effect, leading to higher products (methanol and dimethyl ether) production. The MSW, as raw material, can be converted into sustainable products production applying a complete circular principle in the upgraded input unit, which includes combustion, gasification, and reforming for syngas, and further sustainable liquid or/and gaseous chemicals productions. Municipal solid waste (MSW) with varying amounts of hydrogen can replace conventional natural gas in the production of methanol and dimethyl ether (DME). The MSW with lower hydrogen, including less plastic and more wood amounts, can produce methanol and DME with the same production quality and quantity as with conventional production from natural gas. The MSW with higher hydrogen, including more plastic and less wood amounts, can increase the methanol and DME production. These modifications of methanol and DME production included only the upgraded input unit with decreased temperature in the reactor by 30 °C, which can reduce CO₂ emissions by $3 \cdot 10^6$ kmol a⁻¹. The optimal methanol and DME production amounts from MSW can be increased by 47 % and 16 %, respectively, regarding conventional production from natural gas. The optimal exothermal heat flow rate of methanol and DME reactors can increase the additional steam production by 50 % and 17 %, with regard to conventional production from natural gas. MSW, regardless of the quality amount, can be used efficiently for chemicals and energy production with a lower dependency on natural gas.

List of symbols

- constant slope а
- F - molar flow rate, kmol h⁻¹
- Т - temperature, °C
- X - conversion, %
- heat flow rate, MW φ
- ΔH standard enthalpy of reaction, J mol⁻¹

References

- 1. Lee, R. P., Seidl, L. G., Huang, O., Meyer, B., An analysis of waste gasification and its contribution to China's transition towards carbon neutrality and zero waste cities, J. Fuel Chem. and Techno. 49 (2021) 1057. https://doi.org/10.1016/S1872-5813(21)60093-2
- 2. Hasanzadeh, R., Mojaver, M., Azdast, T., Park, C. B., Polyethylene waste gasification syngas analysis and multi-objective optimization using central composite design for simultaneous minimization of required heat and maximization of exergy efficiency, Energy Convers. Manag. 9 (2021) 114713.
 - doi: https://doi.org/10.1016/j.enconman.2021.114713
- 3. Lopez, G., Artetxe, M., Amutio, M., Bilbao J., Olazar, M., Thermochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals. A review, Renew. Sustain. Energy Rev. 73 (2017) 346. doi: https://doi.org/10.1016/j.rser.2017.01.142
- 4. Messerle, V. E., Mosse, A. L., Ustimenko, A. B., Processing of biomedical waste in plasma gasifier, Waste Manag. 79 (2018) 791. doi: https://doi.org/10.1016/j.wasman.2018.08.048
- 5. Beyene, H. D., Werkneh, A. A., Ambaye, T. G., Current updates on waste to energy (WtE) technologies: A review, Renew. Energy Foc. 24 (2018) 1. doi: https://doi.org/10.1016/j.ref.2017.11.001
- 6. Pan, P., Peng, W., Li, J., Chen, H., Xu, G., Liu, T., Design and evaluation of a conceptual waste-to-energy approach integrating plasma waste gasification with coal-fired power generation, Energy 238 (2022) 121947. doi: https://doi.org/10.1016/j.energy.2021.121947
- 7. Frolov, S. M., Smetanyuk, V. A., Shamshin, I. O., Sadykow, I. A., Koval, A. S., Frolov, F. S., Production of highly superheated steam by cyclic detonations of propane- and methane-steam mixtures with oxygen for waste gasification, Appl. Thermal Eng. 183 (2021) 116195. doi: https://doi.org/10.1016/j.applthermaleng.2020.116195
- 8. Lam, H. L., Ng, W. P. O., Ng, R. T. L., Ng, E. H., Aziz, M. K. A., Ng, D. K. S., Green strategy for sustainable waste-toenergy supply chain, Energy 57 (2013) 4. doi: https://doi.org/10.1016/j.energy.2013.01.032
- 9. Cucchiella, F., D'Adamo, I., Gastaldi, M., Sustainable waste management: Waste to energy plant as an alternative to landfill, Energy Con. Manag. 13 (2017)18. doi: https://doi.org/10.1016/j.enconman.2016.11.012
- 10. Diyoke, C., Gao, N., Aneke, M., Wang, M., Wu, C., Modelling of down-draft gasification of biomass - an integrated pyrolysis, combustion and reduction process, Appl. Thermal Eng. 142 (2018) 444.

doi: https://doi.org/10.1016/j.applthermaleng.2018.06.079

11. Behrend, P., Krishnamoorthy, B., Considerations for waste gasification as an alternative to landfilling in Washington state using decision analysis and optimization, Sustain. Prod. Consum. 12 (2017) 170.

doi: https://doi.org/10.1016/j.spc.2017.07.004

- 12. Nguyen, H. N., Nguyen, P. L. T., Tran, V. B., Zero-waste biomass gasification: Use of residues after gasification of bagasse pellets as CO₂ adsorbents, Thermal Sci. Eng. Prog. 26 (2021) 101080. doi: https://doi.org/10.1016/j.tsep.2021.101080
- 13. Okati, A., Khani, M. R., Shokri, B., Monteiro, E., Rouboa, A., Numerical modelling of plasma gasification process of polychlorinated biphenyl wastes, Energy Rep. 7 (2021) 270. doi: https://doi.org/10.1016/j.egyr.2021.07.123
- 14. Barontini, F., Frigo, S., Gabbrielli, R., Sica, P., Co-gasification of woody biomass with organic and waste matrices in a down-draft gasifier: An experimental and modelling approach, Energy Convers. Manag. 245 (2021) 114566. doi: https://doi.org/10.1016/j.enconman.2021.114566
- 15. Chanthakett, A., Arif, M. T., Khan, M. M. K., Oo, A. M. T., Performance assessment of gasification reactors for sustainable management of municipal solid waste, J. Environ. Manag. 292 (2021) 112661. doi: https://doi.org/10.1016/j.jenvman.2021.112661
- 16. Lee, U., Han, J., Wang, M., Well-to-Wheels Analysis of Compressed Natural Gas and Ethanol from Municipal Solid Waste, ANL/ESD-16/20, Argonne National Laboratory, Argonne (2016).
- 17. Chen, D., Yin, L., Wang, H., He, P., Pyrolysis technologies for municipal solid waste: A review, Waste Manag. 37 (2015) 116. doi: https://doi.org/10.1016/j.wasman.2015.01.022
- 18. Wang, H., Wang, L., Shahbazi, A., Life cycle assessment of fast pyrolysis of municipal solid waste in North Carolina of USA, J. Clean. Prod. 87 (2015) 511. doi: https://doi.org/10.1016/j.jclepro.2014.09.011
- 19. Fujii, M., Fujita, T., Ohnishi, S., Yamaguchi, N., Geng, Y., Park, H. S., Regional and temporal simulation of a smart recycling system for municipal organic solid wastes, J. Clean. Prod. 78 (2014) 208. doi: https://doi.org/10.1016/j.jclepro.2014.04.066
- 20. Soltanieh, M., Azar, K. M., Saber, M., Development of a zero emission integrated system for co-production of electricity and methanol through renewable hydrogen and CO₂ capture, Int. J. Green. Gas Cont. 7 (2012) 145. doi: https://doi.org/10.1016/j.ijggc.2012.01.008
- 21. Puig-Gamero, M., Argudo-Santamaria, J., Valverde, J. L., Sánchez, P., Sanchez-Silva, L., Three integrated process simulation using aspen plus®: Pine gasification, syngas cleaning and methanol synthesis, Energy Convers. Manag. 177 (2018) 416.

doi: https://doi.org/10.1016/j.enconman.2018.09.088

- 22. Tungalag, A., Lee, B. J., Yadav, M., Akande, O., Yield prediction of MSW gasification including minor species through Aspen plus simulation, Energy 198 (2020) 117296. doi: https://doi.org/10.1016/j.energy.2020.117296
- 23. Li., X., Qi, M., Jiu, J., Zhao, D., Wang, X., Research on safety requirements of critical safety instrumented function in coke oven gas to methanol process using aspen simulation, J. Loss Prevent. Process Ind. 60 (2019) 253. doi: https://doi.org/10.1016/j.jlp.2019.05.011
- 24. Borgogna, A., Salladini, A., Spadacini, L., Pitrelli, A., Annesini, M. C., Iaquaniello, G., Methanol production from refuse derived fuel: Influence of feedstock composition on process yield through gasification analysis, J. Clean. Prod. 235 (2019) 1080.

doi: https://doi.org/10.1016/j.jclepro.2019.06.185

- 25. McKetta, J. J., Cunningham, W. A., Encyclopedia of chemical processing and design Vol. 29, Marcel Dekker, New York, (1985), 418-474.
- 26. Kovac Kralj, A., Using applied retrofitting techniques for integration of raw material circulation between industrial plants, J. Environ. Chem. Eng. 9 (2020) 104835. doi: https://doi.org/10.1016/j.jece.2020.104835