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Scientific paper

The Reusage of Different Wastes by Using the Multiple's Effect Technique for Sustainable Gasoline Production

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Abstract

The unused garbage which is accumulating the landfills, such as raw materials, could be reused for synthetic gasoline production. This study presents the multiple's effect technique, which is based on the reusage of different non, party and sorted municipal solid wastes (MSW), or biogas for syngas, converted into synthetic gasoline. The novelties of this technique include a basic multiple's effect parameter (MU_W), which present a level of waste sorting, an effect of oxygen inhibition into different wastes, a simplified mathematical model and simulation with an Aspen Plus® simulator using the retrofitted methanol plan converted into the synthetic gasoline production. This technique includes a circular economy by using a circulated purified flue gas as raw material, co-products of hydrogen and water.

This technique was tested on an existing methanol process, replacing natural gas with different alternatives of wastes or biogas for the synthetic gasoline production. The best alternative was the sorted MSW, which could generate an additional profit of 4.8 MEUR/a, including the garbage and CO_2 emission reductions of $0.106 \cdot 10^6$ t/a and of $0.084 \cdot 10^6$ t/a.

Keywords: Waste; biogas; gasoline production; multiple's effect; circular economy

1. Introduction

Non-renewable petroleum resources could be replaced with gasification of sustainable resources, such as waste, intermediate raw materials, bio-waste, for gasoline or other synthetic fuels` production, using different catalytic converters of Fischer-Tropsch (FT) synthesis, fixed-bed reactors, plasma etc.

The Introduction includes in detail the literatures of the research of different synthetic production, such as gasoline and fuels, including the gasification technique. Lu et al. contributed the new research of the selective conversion of CO and H_2 to gasoline products (iso-paraffin and olefin), including the demonstrated effective H-USY zeolite supported nano-cobalt bifunctional catalysts for this catalytic reaction, which are prepared by the novel physical sputtering process. Compared with H-Mor, H-Beta and other zeolite supported catalysts, the H-USY zeolite supported cobalt catalyst shows the clearest promotional effect on the activity of Fischer-Tropsch synthesis.[1] Javed et al. presented new research of the high CO_2 selectivity of Fe-based Fischer-Tropsch microcapsule catalysts for gasoline production. The novelties of this research were the included Silicalite-1 shell 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, including $CO_2$ selectivity, was decreased by suppressing the water-gas shift reaction activity. All zeolite supported Fe-based catalysts showed significantly high gasoline range hydrocarbons` selectivity (about 60%).[2]

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. The HZSM-5/MnAPO-11 composite showed the highest gasoline yield and iso-paraffin selectivity, due to the presence of more mesopores and moderate acid sites.[3] Lu and co-workers stated the study of the production of gasoline-range hydrocarbons from nitrogen-rich syngas over an Mo/HZSM-5 bi-functional catalyst in a bench-scale continuous stainless steel fixed-bed reactor with different reaction conditions. The reaction conditions, i.e., temperature, pressure and gas hourly space velocity, affected the hydrocarbon selectivity significantly.

The novelties included that the nitrogen-rich syngas can be converted into gasoline-range hydrocarbon over Mo/HZSM-5 in one step, and high nitrogen content in syngas was found to affect liquid hydrocarbon distribution.[4]

Zhang et al. developed the upgrade of the Ni/ASA catalysts with various Ni contents, which were prepared successfully through a wet impregnation method for the gasoline-range hydrocarbons` production from the oligomerization of olefins-rich bio-syngas. The studies of this research, which contained the catalytic performance, may be relevant to the balance between acid and nickel ion sites and fuels, and the high Ni loading amount of Ni/ASA may enhance the hydrogenation reaction of olefins.[5] Liu and co-workers presented the novelties of the catalytic performance with cobalt nanoparticles embedded into zeolite crystals for the direct synthesis of gasoline from syngas. The highlights of the research were series CoZ-xN catalysts with a novel cobalt-embedded zeolite structure, the coincidence of the rate of silica dissolving and zeolite growth was important, and the formation mechanism was proposed of the catalyst.[6]

Martin and Cirujano contributed the new research of the multifunctional heterogeneous catalysts for the tandem CO_2 hydrogenation Fischer-Tropsch synthesis of gasoline, including several iron-containing multifunctional catalysts based on metal oxides, carbon or zeolite materials. The novelties of this research were the included advantages of metal oxides, carbons or zeolites as support of the active Fe-catalyst, including Fe-support interactions, and the electronic and geometric properties of the active sites.[7] Li et al. presented the new research of the conversion of dimethyl ether to gasoline, using a series of nanocrystal H[Fe,Al]ZSM-5 zeolite samples with different SiO_2/Al_2O_3 ratios with a hydrothermal method. The highlights contained zeolite acidity, which was related with the synergistic effect of Al- and Fe-based acid sites, and a catalyst with an SiO_2/Al_2O_3 ratio of 45 exhibited the best catalytic performance for a dimethyl ether to gasoline reaction.[8] Su et al. developed the upgrade of the catalysts for dimethyl ether conversion to iso-paraffin-rich gasoline, including nanosized ZSM-5 (NZ5) and zinc isomorphously substituted ZSM-5 ([Zenial]NZ5) zeolites with different Si/Me ratios in initial gels (Me = Al or Al and Zn). The novelties contained iso-paraffin selectivity in gasoline hydrocarbons, which was enhanced by Zn incorporation, and $ZnOH^+$ species showed the excellent hydrogenation activity for a dimethyl ether to gasoline reaction.[9]

Magomedova et al. proposed the upgrade of the syngas-to-gasoline technology for the synthesis of liquid hydrocarbons through oxygenates (methanol and dimethyl ether), giving a light synthetic oil with a low concentration of aromatic compounds (8–16 wt %). The study contained dimensionless criteria for heat and mass transfer, which were used for plant scaling, and the operation was carried out of a pilot plant for syngas to low-aromatic gasoline via DME.[10] Szczygieł and Kułażyński contributed the research of the gasoline production from dimethyl ether and methanol, including thermodynamic limitations of synthetic fuel production. Thermodynamic analysis of the classic methanol-to-gasoline process that employs CO as a raw material allowed a comparison with the modified version of the process, assessment of their effectiveness, and deductions concerning the possible benefits and losses resulting from replacing CO with carbon dioxide. The use of CO as a raw material was clearly more favourable in terms of the tendency towards a spontaneous reaction.[11]

Rabah presented the upgrade of syngas production from biomass gasification as a potential energy source for power generation and manufacturing synthetic gasoline and diesel via Fischer-Tropsch synthesis. The operating conditions under which the objective function and the constraint were satisfied were the steam to biomass ratio, equivalent ratio, and gasification temperature.[12] Shiying et al. contributed the upgrade of the dual-stage entrained flow gasification and CO_2 cycling in biomass-to-gasoline/diesel, including design and techno-economic analysis. The dual-stage entrained flow gasification avoided separate torrefaction of biomass feedstock and provided higher cold gas efficiency, which made the addition of steam as a gasification agent feasible. The high efficiency of Fe-based slurry-phase Fischer-Tropsch synthesis reactors also enhanced the gasoline production.[13] Borugadda et al. explored the new research of the techno-economic and life-cycle assessment of the integrated Fischer-Tropsch process in the ethanol industry for bio-diesel and bio-gasoline production, using syngas obtained from the gasification of dry distillers' grain. The lab-scale experiment using pelletised promoted iron supported on Carbon Nano Tubes (Fe/CNT) was used to simulate a plant for the production of 1000 kg of syncrude/h.[14]

Mascal and Dutta presented the study of the synthesis of highly-branched alkanes, such as iso-alkanes and cycloalkanes, for renewable gasoline production from bio-oil and raw biomass using chemo-catalytic methods. Gasoline can be made from biomass pyrolysis gas via the Fischer-Tropsch or methanol-to-gasoline processes, as well as the refining of bio-oil, raw biomass, etc.[15] Hnich et al. investigated the study of the life cycle sustainability performance of synthetic diesel and gasoline from Tunisian date palm waste, and compared it with that of conventional fossil fuels. The potential environmental impacts of the biomass-to-liquid system were concluded to be associated mainly with direct emissions and the system's demand for electricity and oxygen.[16] Wang et al. designed the upgrade of the pilot plant for biomass converted to liquid fuels, including gasification, direct synthesis of dimethyl ether (DME) and DME to gasoline. The operating results showed that both the pressure and gas hourly space velocity (GHSV) not only influenced the CO conversion and the DME yield, but also had a significant effect on the manipulation of the reaction heat in the adiabatic reactor. High pressure and low GHSV favoured the high CO conversion

and the DME yield.[17] Navas-Anguita et al. presented the study of the simulation and life cycle assessment of a biogas-to-liquid plant for the coproduction of synthetic fuels (diesel and gasoline) and electricity. The system comprised a biogas dry reforming process to produce syngas, Fischer-Tropsch synthesis, and a combined-cycle process. In particular, the life-cycle environmental profile of synthetic biodiesel as the main product of the biogas-to-liquid plant was calculated, and compared with that of conventional diesel.[18]

Bahri et al. presented the novelties of the synergistic effect of a bifunctional mesoporous ZSM-5 supported Fe-Co catalyst for selective conversion of syngas with a low riblet ratio into synthetic fuel. The Fe-Co bimetallic active metals were loaded on mesoHZSM-5 with varying Fe-Co ratios, with a constant total metal loading of 30%, using the sonication process to increase active metal dispersion. The catalytic activity was tested in the laboratory scale fixed bed reactor.[19] Aluha and Abatzoglou contributed the study of the synthetic fuels from 3-φ Fischer-Tropsch synthesis using syngas feed and novel nanometric catalysts. The research presented the novel carbon-supported Co-Fe bimetallic catalysts which were synthesised through plasma. All the catalysts reduced in CO or H_2 showed equal activity of about 40% CO conversion.[20] Ali et al. defined the new research of the direct synthesis of liquid fuels and aromatics from syngas using the Fischer-Tropsch synthesis reaction on hybrid catalysts containing a highly ordered mesoporous FeZrOx bimetal oxide mixed physically with Mo-modified ferrierite (Mo/HFER). The hybride FeZrOx-Mo/HFER catalyst showed synergistic effects with a higher CO conversion to liquid fuels and aromatics. Optimal hydrophobicity and acidic sites on the Mo/HFER were responsible for the enhanced catalytic stability.[21]

Selvatico et al. obtained the upgrade of the kinetic model, based on Langmuir–Hinshelwood–Hougen–Watson for the Fischer-Tropsch synthesis of fuel, converting it into a well-established industrial process simulator. A low temperature Fischer-Tropsch process was modelled for the middle distillate production.[22] Wu et al. reported the novelties of the reformation of n-pentane (C_5H_{12}) using methane (CH_4) or carbon dioxide (CO_2) in a temperature-controlled dielectric barrier discharge reactor to produce hydrogen and clean carbon-based fuels, by using low-temperature plasma. A mechanistic study suggested that electron-induced chemistry dominates C_5H_{12} and the added gas conversion, whereas the thermochemistry controls the product distribution.[23] Liu and Larson described the study of two routes to produce liquid hydrocarbon fuels from solids via synthesis gas, Fischer-Tropsch (FT) synthesis and methanol-to-gasoline (MTG). This study compared the performance and cost of the Fischer-Tropsch and MTG processes on a self-consistent basis. In particular, FT and MTG production from coal and coal/biomass cofeeds were compared, including detailed mass, energy and carbon balances.[24] Dutta et al. provided the new research of an overview of producing fuel precursors from biomass components, and their catalytic transformation into aviation-, diesel-, and gasoline-range hydrocarbon fuels (HCFs), including strategic applications of various organic transformations for the molecular design. Emphasis was also given to the process conditions and details of the catalysts employed in these processes. The synthesis of HCFs was warranted to ensure the high quality and homogeneity of the properties, including minimizing the energy input.[25]

Santos and Alencar presented the upgrade of the syngas production from biomass gasification and its subsequent conversion into fuels through the Fischer-Tropsch synthesis. This study included a debate on the main catalysts, industrial process requirements, and chemical reaction kinetics and mechanisms of Fischer-Tropsch synthesis. Lignocellulosic material of biomass would be considered a low-cost feedstock to the liquid biofuel production on a large scale.[26] Campanario and Ortiz contributed the upgrade of the Fischer-Tropsch biofuels` production from syngas obtained by supercritical water reforming of the bio-oil aqueous phase, including the produced maximum biofuels and electrical power. The highlights of this research contained the upgraded production of syngas by using water-gas-shift, dry reforming and Fischer-Tropsch (FT) reactors, and followed the optimal conditions in the FT reactor: 220 °C, 40 bar and H_2/CO ratio of 1.70.[27]

Gharibi et al. contributed the study of the metaheuristic particle swarm optimization for enhancing energetic and exergetic performances of hydrogen energy production from plastic waste gasification. The novelties contained were multi-objective particle swarm optimization for plastic gasification, using grey relational analysis, and achieving lower heating for the polypropylene gasification and higher efficiency of cold gas.[28] Gharibi et al. prepared a few novel studies to predict polyethylene waste performance in gasification using multilayer perceptron (MLP) machine learning algorithms and interpreting them using multi-criteria decision-making methods. The main aims of this study were to develop MLP artificial neural networks and regression models to predict polyethylene gasification performance with high accuracy.[29] Mojaver et al. prepared the novel thermodynamic assessment of an integrated solid oxide fuel cell with a steam biomass gasification and high-temperature sodium heat pipes for combined heating and power production. The modelling and analysis of the system were performed using mass and energy conservation laws and equilibrium constants. The results of the extended model were confirmed by the experimental results.[30] Mojaver et al. defined the multi-objective optimization using response surface methodology and exergy analysis of a novel integrated biomass gasification, solid oxide fuel cell and high-temperature sodium heat pipe system. Response surface methodology was utilised to investigate the effect of the decision variables on the responses, i.e., the electrical power and the exergy effi-

ciency.[31] Hasanzadeh and Azdast defined the novel machine learning utilisation on air gasification of polyethylene terephthalate waste. The machine learning algorithms had good performance in predicting the performance. The models for lower heating values and cold gas efficiency showed excellent accuracy.[32] Doniavi et al. improved the efficiency of polyethylene gasification. This research was focused on the energy, exergy, and environmental impact in relation to the material conditions. These models were then optimised using a general algebraic modelling system. The results indicated that the ideal conditions consist of 84.40 % carbon content, 15 % hydrogen content, and no oxygen or nitrogen content.[33]

Hasanzadeh and Abdalrahman defined a novel research, in which it was recognised that the processing parameters have a crucial impact on the assessment of polyvinyl chloride waste gasification. The study used data collected through a validated thermodynamic model, and three different regression models were tested and compared in detail. Cold gas efficiency and normalised carbon dioxide emission were predicted using linear, quadratic, and quadratic with interaction algorithms.[34] Khalilarya et al. contributed a new research, which combined a heat and power system which consisted of a gasifier, a micro gas turbine, an organic Rankine cycle, a heat exchanger and domestic heat recovery. Air, steam, and oxygen were considered as different gasification mediums. The Taguchi approach was employed to optimise the generated power in the air, steam and oxygen medium cases.[35] Mojaver et al. researched the novel system of a fluidised bed gasifier with steam as the gasifying agent. The synthesis of gas composition and efficiencies of the system were investigated with respect to different biomasses considered as gasification fuels. The results indicated that the molar fractions of hydrogen and carbon dioxide were increased, and the molar fraction of carbon monoxide was reduced with the steam to biomass ratio.[36]

Hasanzadeh et al. improved the gasification model of polyethylene waste, by using the Gibbs free energy minimisation and 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 reactions.[37] Mojaver et al. compared the performances between biomass and plastic waste gasification. The important novelty and contribution of this study was the analytical hierarchy process/technique for order performance by similarity to the ideal solution coupled method that was employed in gasification of conventional biomass and plastic waste, to prioritise the considered criteria and to select the best feedstock for gasification.[38] Mojaver et al. presented a new study, in which the steam gasification was modelled of polyethylene, polypropylene, polycarbonate and polyethylene terephthalate waste. The effects of key features, including the steam to plastic waste ratio, temperature, moisture content and pressure, were assessed on hydrogen-rich syngas compositions, and the exergy destruction rate. The Taguchi approach was utilised to investigate and optimise the process. The findings revealed that the gasification of polypropylene waste led to the highest hydrogen production at all the processing conditions.[39]

In this study, the gaps in the literature were covered about the usage of the different wastes for syngas, and further into sustainable synthetic gasoline productions. The novelties of this study present the multiple's effect technique, which uses the basic multiple's effect parameter (MU_W) for the different level of waste sorting, including the effect of oxygen inhibition into different wastes. The contributions of this research include the circular economy by using a simple mathematical model for different municipal solid wastes (MSW) from non-sorted to sorted, or biogas. The objectives of this study contain the applied composition data of different wastes and the simulation model by using the Aspen Plus® simulator.

2. The Multiple's Effect Technique

The nature source, such as petroleum, would be replaced by the non-sorted (WNS), partially sorted (WPS), or sorted (WS) wastes from landfill or biogas for the sustainable synthetic gasoline production, by using the multiple's effect technique. This study presents the multiple's effect technique, which is based on the reusage of different MSW or biogas, supported by a mathematical model and the Aspen Plus® simulator for syngas converted into synthetic gasoline. This technique adapts the replacement of the existing methanol process to synthetic gasoline production, by using the same process units. The simple mathematical model uses the basic multiple's effect parameter (MU_W), which presents the level of waste sorting (MU_W; $MU_{WNS} = 0$; $MU_{WPS} = 1$; $MU_{WS} = 2$). The sorted wastes include the highest value of the multiple's effect parameter. The multiple's effect parameter allows easy calculation of the product's production and other important amounts from different wastes, including the sustainable co-produced raw materials, such as water, hydrogen and flue gas.

The synthetic gasoline would be produced from the different MSW by using the basic process units (Fig.1), which are very similar to methanol production, such as gasification of MSW (G-MSW), reforming (Ref), cooling (Coo), the first water removing (Rem1-H_2O), compressing (Com), preheating to the reaction's temperature (PreH-R), reacting (R), the first crude product cooling (Coo1-SG), the second water removing (Rem2-H_2O), the second crude product cooling (Coo2-SG), the liquid product's purification (P-SG), and hydrogen separation from nonreacted gas with a pressure swing adsorption column (PSA-H_2). The adapted process units include the optimal parameters,

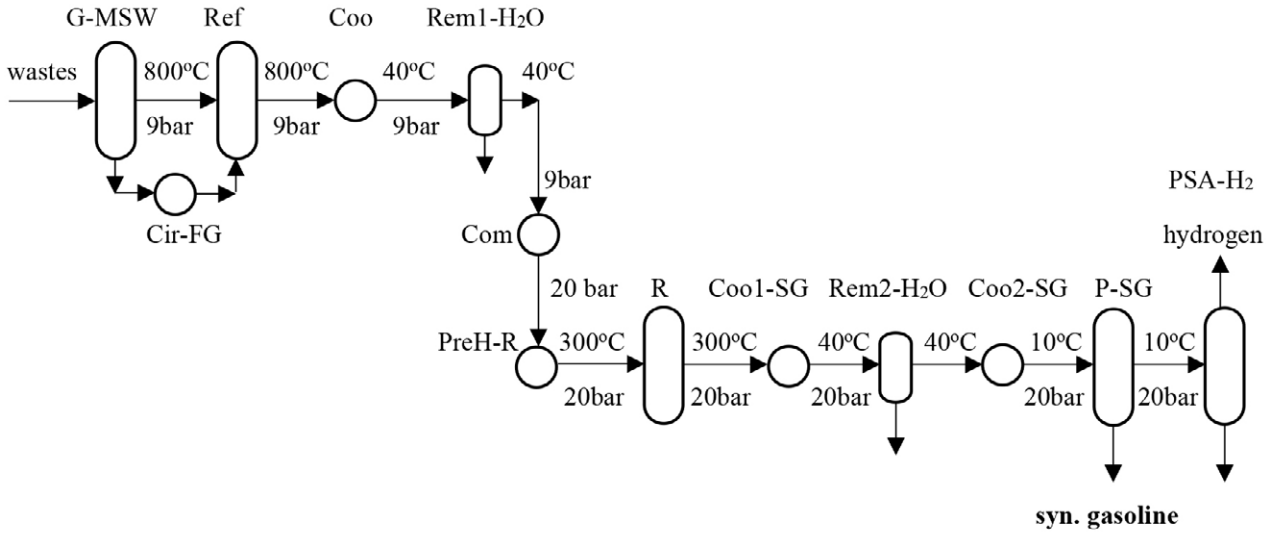


Figure 1: The process flow-diagram of the synthetic gasoline production for the different wastes including the parameters.

effects and characteristics (Fig. 1). MSW should be gassed before reforming (G-MSW). The flue gas of gasification, such as raw material, would be purified and circulated into reforming (Cir-FG).

Different municipal solid wastes (MSW) would be converted into syngas by using combustion, gasification and reforming. The purified flue gas of combustion (without particles, NO_x, SO_x, oxygen and nitrogen), including steam and carbon dioxide, is transported circularly into the gasification-reforming part, without releasing the outlet exhaust into the atmosphere. The purified flue gas is used as sustainable raw material, which would reduce the emissions and amount of clean steam. The different MSW are presented with the basic components of C, H_2, O_2 and N_2. The non-sorted MSW include lower plastics and woods (as components of C and H_2), because of a higher content of rubbers, leathers, textiles, papers, etc (as components of O_2 and N_2, too). The sorted MSW includes more plastics and woods because of the lower content of rubbers, leathers, textiles, paper, etc. The carbon and hydrogen ($F_{C,W}$, $F_{H2,W}$) are affected mostly by the reactions. The amount of oxygen is reducing the production of the synthetic gasoline and the neutral nitrogen is filling the process flows. The purified and circulated flue gas contains the components of CO_2 and H_2O, representing a circular economy system.

The basic simplified endothermic reaction of Re1 takes place into the reformer (Ref), which is producing syngas with a yield of carbon monoxide ($Y_{CO,Re1}$ = 0.999) mostly from the waste's carbon. The circulated carbon dioxide from the flue gas (FG) is converted to carbon monoxide with 80% conversion of Re2 reaction ($X_{FG,CO,Re2}$ = 0.8), and the remaining 20% (or (1 – $X_{FG,CO,Re2}$)) flows into the product's reactor (R).

$$C + H_2 + H_2O \leftrightarrows CO + H_2 + H_2O \quad \text{(Re1)}$$

$$CO_2 + H_2 \leftrightarrows CO + H_2O \quad \text{(Re2)}$$

The syngas converts to the synthetic gasoline (SG) from wastes into the reactor (R) by using two basic exothermic reactions (Re3, Re4) with the conversions of CO and CO_2 ($X_{CO,Re3}$ = 0.996, $X_{CO2,Re4}$ = 0.56).

$$8\ CO + 17\ H_2 \leftrightarrows C_8H_{18} + 8\ H_2O \quad \text{(Re3)}$$

$$8\ CO_2 + 25\ H_2 \leftrightarrows C_8H_{18} + 16\ H_2O \quad \text{(Re4)}$$

The carbon molar flow rates ($F_{C,W}$) of different wastes (non-sorted, WNS or partially-sorted, WPS, or sorted, WS; W = WNS,WPS,WS) are dependent on the lowest inlet ($F_{C,WNS}$ = 600 kmol/h) and the difference in carbon amounts (ΔF_C = 100 kmol/h), including the multi-

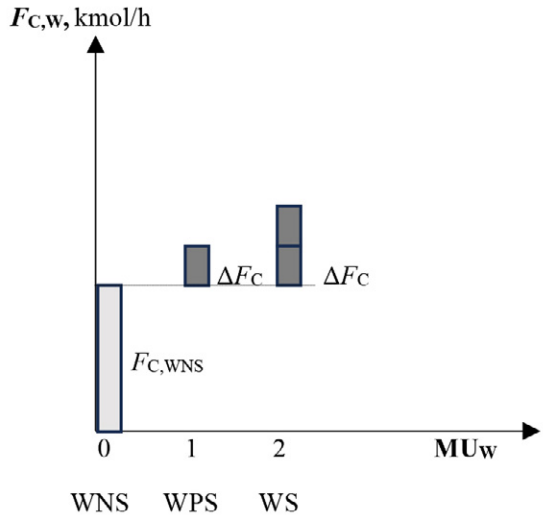


Figure 2: Flow-diagram of the graphical presentation the carbon molar flow rates ($F_{C,W}$) for different wastes by using the multiple's effect technique.

ple's effect parameter (MU_W; MU_{WNS} = 0; MU_{WPS} = 1; MU_{WS} = 2; Eq. 1).

$$F_{C,W} = F_{C,WNS} + \Delta F_C \cdot MU_W \quad W = WNS, WPS, WS \tag{1}$$

The carbon molar flow rates ($F_{C,W}$) of different wastes can be presented graphically by using the multiple's effect technique (Fig. 2).

The reacted synthesised gasoline molar flow rate ($_rF_{SG,W}$; Eq. 4) into reactor (R) from different wastes is dependent on the reactions (Re1 and Re3) of CO reacting ($_rF_{SG,Re3,W}$; Eq. 2) and the circulated CO_2 molar flow rate from the flue gas ($F_{FG,CO2}$ = 240 kmol/h), which takes place at the reactions (Re2 and Re3) of CO and CO_2, reacting for using the reaction of Re4 ($_rF_{SG,FG}$; Eq. 3), including eight gasoline's molecules (M = 8).

$$_rF_{SG,Re3,W} = (F_{C,W} \cdot Y_{CO,Re1} \cdot X_{CO,Re3})/M \quad W = WNS, WPS, WS \tag{2}$$

$$_rF_{SG,FG} = [(F_{FG,CO2} \cdot X_{FG,CO,Re2} \cdot X_{CO,Re3}) + (F_{FG,CO2} \cdot (1 - X_{FG,CO,Re2}) \cdot X_{CO2,Re4})]/M \tag{3}$$

$$_rF_{SG,W} = (_rF_{SG,Re3,W} + _rF_{SG,FG}) \quad W = WNS, WPS, WS \tag{4}$$

The reacted synthesised gasoline ($_rF_{SG,W}$) is lost because of the oxygen in the non-sorted waste and the product's cleaning (P-SG) by 4% (Eq. 5; $L_{P\text{-}SG,W}$ = 0.04). The oxygen in the non-sorted waste acts as an inhibitor, with the different losses dependent on the sorting levels ($L_{O2,WNS}$ = 0.1, $L_{O2,WPS}$ = 0.05, $L_{O2,WS}$ = 0.0). The total produced synthesised gasoline ($F_{SG,W}$) can be calculated by using Equation 5.

$$F_{SG,W} = _rF_{SG,W} \cdot (1 - L_{P\text{-}SG,W}) \cdot (1 - L_{O2,W}) \quad W = WNS, WPS, WS \tag{5}$$

The hydrogen molar flow rate ($F_{H2,W}$; Eq. 6) of different wastes, such as coproduct, separates from nonreacted gas using the pressure swing adsorption column (PSA-H_2), which is calculated dependent on the lowest inlet ($F_{H2,WNS}$ = 1600 kmol/h), the difference of the inlet ($\Delta F_{H2,W}$ = 100 kmol/h), the lowest reacted amount ($_rF_{H2,WNS}$ = 1334 kmol/h) and the reacted difference of the hydrogen amount (Δ_rF_{H2} = 87 kmol/h), including the multiple's effect parameter (MU_W; MU_{WNS} = 0; MU_{WPS} = 1; MU_{WS} = 2).

$$F_{H2,W} = (F_{H2,WNS} + \Delta F_{H2} \cdot MU_W) - (_rF_{H2,WNS} + \Delta_rF_{H2} \cdot MU_W) \quad W = WNS, WPS, WS \tag{6}$$

The produced water molar flow rate ($F_{H2O,W}$; Eq. 7) through the plant is determined with the lowest produced ($F_{H2O,WNS}$ = 815 kmol/h) and difference (ΔF_{H2O} = 97 kmol/h) amounts, including the multiple's effect parameter (MU_W; MU_{WNS} = 0; MU_{WPS} = 1; MU_{WS} = 2).

$$F_{H2O,W} = F_{H2O,WNS} + \Delta F_{H2O} \cdot MU_W \quad W = WNS, WPS, WS \tag{7}$$

The Re1 reaction needs the inlet steam molar flow rate ($F_{H2O,Re1,W}$; Eq. 8) deriving from the flue gas, which is dependent on the lowest ($F_{H2O,re1,WNS}$ = 350 kmol/h) and difference ($\Delta F_{H2O,Re1}$ = 100 kmol/h) amounts, including the multiple's effect parameter (MU_W; MU_{WNS} = 0; MU_{WPS} = 1; MU_{WS} = 2).

$$F_{H2O,Re1,W} = F_{H2O,Re1,WNS} + \Delta F_{H2O,Re1} \cdot MU_W \quad W = WNS, WPS, WS \tag{8}$$

The simplified energy analysis includes the needed energy of gasification (ϕ_G = 25 MW), which is the same for all wastes, and reforming ($\phi_{ref,W}$; Eq. 9), including the available energy of the product's reactor ($\phi_{R,W}$; Eq. 10). The endothermal heat flow rate of the reformer ($\phi_{ref,W}$; Eq. 9) expresses with the lowest ($\phi_{ref,WNS}$ = 24 MW) and difference ($\Delta\phi_{ref}$ = 3.7 MW) of the heat flow rates, including the multiple's effect parameter (MU_W; MU_{WNS} = 0; MU_{WPS} = 1; MU_{WS} = 2).

$$\phi_{ref,W} = \phi_{ref,WNS} + \Delta\phi_{ref} \cdot MU_W \quad W = WNS, WPS, WS \tag{9}$$

The exothermal heat flow rate of the product's reactor ($\phi_{R,W}$; Eq. 10) is dependent on the lowest ($\phi_{R,WNS}$ = 37 MW) and difference ($\Delta\phi_R$ = 4.3 MW) of the heat flow rates, including the multiple's effect parameter (MU_W; MU_{WNS} = 0; MU_{WPS} = 1; MU_{WS} = 2).

$$\Phi_{R,W} = \phi_{R,WNS} + \Delta\phi_R \cdot MU_W \quad W = WNS, WPS, WS \tag{10}$$

The objective function of the retrofit using different MSW (OBF_W; Eq 11) maximises the additional profit. The additional income accounts for the product (*In*SG; with price of Co_{SG} = 10 EUR/kmol) and co-product purchases (*In*H2; with price of Co_{H2} = 3 EUR/kmol). The same applied costs, independent of the wastes, include the cost of the retrofit (Cret = 5 MEUR/a, including a new catalyst), the cost of gasification (Cgas = 3 MEUR/a), and the cost of the circulated flue gas (CFG = 1 MEUR/a). The applied costs, dependent on the wastes, contain the cost of sorting (Csor,W; Eq. 12) and the cost of energy analysis (Cen,W; Eq. 13), using 8,000 operating hours (O) per year.

$$OBF_{W\ =\ In}SG + InH2 - (Cret + Cgas + CFG) - (Csor,W + Cen,W) = F_{SG,W} \cdot Co_{SG} \cdot O + F_{H2,W} \cdot Co_{H2} \cdot O - (C_{ret} + C_{gas} + C_{FG}) - (C_{sor,W} + C_{en,W}) \quad W = WNS, WPS, WS \tag{11}$$

The cost of sorting includes the constant (C_{sor} = 1 MEUR/a) and variable parts, which is dependent on the difference (ΔC_{sor} = 0.4 MEUR/a) cost, including the multiple's effect parameter (MU_W; MU_{WNS} = 0; MU_{WPS} = 1; MU_{WS} = 2).

$$C_{sor,W} = C_{sor} + \Delta C_{sor} \cdot MU_W \quad W = WNS, WPS, WS \tag{12}$$

The cost of energy analysis determines the difference between endothermal ($\phi_{ref,W}$) and exothermal ($\Phi_{R,W}$) heat flow rates, temperatures into both units (T_{ref} = 800 °C and T_R = 300 °C) and the energy cost (Co_{en} = 100 EUR/(MW °C a).

$$C_{en,W} = \phi_{ref,W} \cdot T_{ref} \cdot Co_{en} - \phi_{R,W} \cdot T_R \cdot Co_{en} \quad W = WNS, WPS, WS \tag{13}$$

2. 1. The Multiple's Effect Technique of Biogas

The simple mathematical model of biogas (BG) is even more simplified because of its not so different composition as the MSW, therefore, is not necessary use the multiple's effect parameter. The biogas contents are mostly components of methane and carbon dioxide ($F_{CH4,BG}$, $F_{CO2,BG}$). The flow-diagram of synthetic gasoline production from biogas is very similar to the flow-diagram from different wastes, only without the circulated flue gas and gasification, which is replaced with preheating biogas (preH-BG; Fig. 3). The basic reaction of Re5, producing syngas from biogas (as molar flow rates of $F_{CH4,BG}$ and $F_{CO2,BG}$) takes place during the reformer (Ref), with yields of the carbon monoxide from methane ($Y_{CO,Re5,BG}$ = 0.7).

$$CH_4 + H_2O \leftrightarrows CO + 3H_2 \tag{Re5}$$

The syngas converts to synthetic gasoline from biogas into the reactor (R) by using two basic exothermic reactions (Re3, Re4), with the conversions of CO and CO_2 ($X_{CO,Re3,BG}$ = 0.996, $X_{CO2,Re4,BG}$ = 0.56) .

The reacted synthesised gasoline molar flow rate ($_rF_{SG,BG}$; Eq. 16) from biogas ($F_{CH4,BG}$ = 650 kmol/h and $F_{CO2,BG}$ = 350 kmol/h) takes place during the reactions of Re3 (Eq. 14) and Re4 (Eq. 15).

$$_rF_{SG,Re3,BG} = (F_{CH4,BG} \cdot Y_{CO,Re5,BG} \cdot X_{CO,Re3,BG})/M \tag{14}$$

$$_rF_{SG,Re4,BG} = (F_{CO2,BG} \cdot X_{CO2,Re4,BG})/M \tag{15}$$

$$_rF_{SG,BG} = {}_rF_{SG,Re3,BG} + {}_rF_{SG,Re4,BG} \tag{16}$$

The reacted synthesised gasoline ($_rF_{SG,BG}$) from biogas is lost into the product's purification unit (P-SG) by 4% ($L_{P\text{-}SG,BG}$ = 0.04), therefore, the amount of produced synthesised gasoline ($F_{SG,BG}$) is lower (Eq. 17).

$$F_{SG,BG} = {}_rF_{SG,BG} \cdot (1 - L_{P\text{-}SG,BG}) \tag{17}$$

The other processed and energetic parameters are not so variable, mostly because of the constant composition of the biogas.

3. Case Study of The Multiple's Effect Technique for the Different Wastes

The synthetic gasoline production of different municipal solid wastes (MSW) has been tested by using the multiple's effect technique, which was adapted from the existing methanol process for synthetic gasoline production, because of very similar process units. The case study

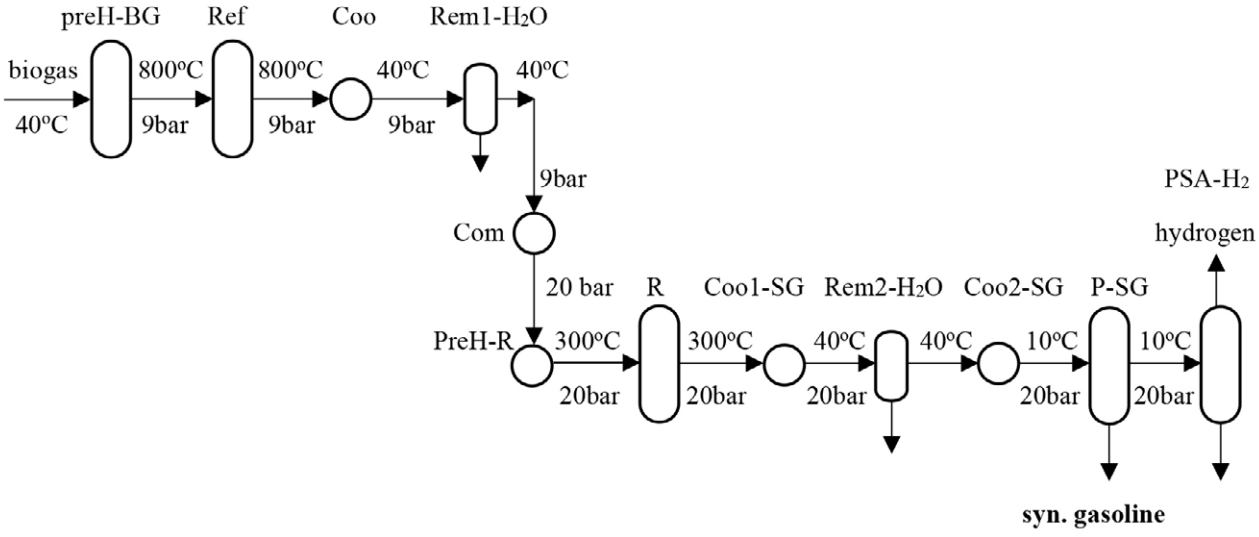


Figure 3: The process flow-diagram of the synthetic gasoline production for biogas including the parameters.

of simulated synthetic gasoline production was undertaken using the optimal parameters, effects and characteristics from Figure 1, by using the Aspen Plus® simulation. The synthetic gasoline production[3] from waste was simulated by using the verified real thermodynamic method and rector model, such as Grayson and Requil from the Aspen Plus® simulator. The economic analyses were included the applied purchase and operation costs for the retrofit.

The total produced synthesised gasolines from non-sorted to sorted wastes were determined as the amounts of 87, 104 and 121 kmol/h ($F_{SG,WNS}$, $F_{SG,WPS}$, $F_{SG,WS}$; Eqs 1–5). The coproduct of hydrogen molar flow rates were estimated as the amounts of 266, 279 and 292 kmol/h ($F_{H2,WNS}$, $F_{H2,WPS}$, $F_{H2,WS}$; Eq. 6).

The produced water molar flow rates were assessed as the amounts of 815, 912 and 1009 kmol/h ($F_{H2O,WNS}$, $F_{H2O,WPS}$, $F_{H2O,WS}$; Eq. 7). The inlet steam molar flow rates were calculated as the amounts of 350, 450 and 550 kmol/h ($F_{H2O,Re1,WNS}$, $F_{H2O,Re1,WPS}$, $F_{H2O,Re1,WS}$; Eq. 8).

The reformer endothermal heat flow rates were expressed as energies of 24, 27.7 and 31.4 MW ($\phi_{ref,WNS}$, $\phi_{ref,WPS}$, $\phi_{ref,WS}$; Eq. 9). The reactor exothermal heat flows were estimated as energies of 37, 41.3 and 45.6 MW ($\phi_{R,WNS}$, $\phi_{R,WPS}$, $\phi_{R,WS}$; Eq. 10).

The objective function of the retrofit generated profits of 2.2, 3.6, and 4.8 MEUR/a using the non, partially and sorted MSW for synthesised gasoline productions (Eqs 11-13). The best alternative was the synthesised gasoline production of $0.127 \cdot 10^6$ t/a from sorted MSW, because of the highest profit of 4.8 MEUR/a and the garbage reduction of $0.106 \cdot 10^6$ t/a into the landfill, including the flue gas and CO_2 emission reductions of $0.164 \cdot 10^6$ and $0.084 \cdot 10^6$ t/a. The hydrogen and processed water coproducts of $4.6 \cdot 10^3$ t/a and $0.145 \cdot 10^6$ t/a could justify the execution too. This alternative could be used to reduce the Russian natural gas and petroleum inflows into the industries and transports.

3. 1. Case Study of the Multiple's Effect Technique for the Biogas

The simple mathematical model of biogas (BG) was simulated by using the parameters from Figure 3, which were contained mostly in the methane and carbon dioxide ($F_{CH4,BG}$ = 650 kmol/h and $F_{CO2,BG}$ = 350 kmol/h). The synthesised gasoline ($F_{SG,BG}$) produced was the amount of 78 kmol/h (Eqs. 14-17). The coproducts of hydrogen and processed water produced amounts of 120 and 780 kmol/h ($F_{H2,BG}$, $F_{H2O,BG}$). The Re5 reaction needed the amount of 950 kmol/h ($F_{H2O,Re5,BG}$). The preheating, endothermal and exothermal heat flow rates were the energies of 11, 37 and 27 MW ($\phi_{preH\text{-}BG}$, $\phi_{ref,BG}$, $\phi_{R,BG}$).

The objective function of the retrofit generated a profit of 1.0 MEUR/a for synthesised gasoline production of $0.08 \cdot 10^6$ t/a from biogas using Equation 11, without the costs of gasification, circulated gas and sorted waste, with those replacing with cost of biogas (C_{BG} = 1 MUR/a).

The comparisons between all alternatives of different raw materials were collected into Table 1, which included the data of the synthetic gasoline production. The distinctions between production and energetic molar and heat flow rates were fairly linear, because of using the multiple's effect parameter (MU_W), which was also the best approximation of the simulated data.

4. Conclusion

The study of synthetic gasoline production from different wastes, such as non, or partially, or sorted wastes, or biogas, would be one of the alternatives of petroleum compensation and reductions of the CO_2 emission and the wastes into landfill, by using the multiple's effect technique. This technique bases on the multiple's effect parameter (MU_W), which presents the level of waste sorting (MU_W; MU_{WNS} = 0; MU_{WPS} = 1; MU_{WS} = 2), and the sorted waste represents the highest value of the multiple's effect parameter. The multiple's effect parameter could simplify the amount calculations of the product and co-product productions, including the energies into process units and the effect of oxygen inhibition into different wastes. The sustainable synthetic gasoline production would be worked according to the principle of the circular economy, including that the purified flue gas of gasification would be circulated back into the process.

The calculations of all the presented alternatives were performed by using the presented technique, and confirmed that the waste should be separated, because of the environmental reasons and more profitable synthetic gasoline production. The sustainable synthesised gasoline production from sorted waste generated the highest additional profit of 4.8 MEUR/a, synthesising the amount of 0.127 10^6 t/a of synthetic gasoline. The garbage from landfill was reduced by 0.106 10^6 t/a by using sustainable

Table 1: The important results comparisons between all alternatives.

Raw. material	F_{SG}, kmol/h	F_{H2}, kmol/h	F_{H2O}, kmol/h	ϕ_{ref}, MW	ϕ_R, MW	Incomes, MEUR/a	Costs, MEUR/a	Profit, MEUR/a
WNS	87	266	815	24.0	37.0	13.3	11.1	2.2
WPS	104	279	912	27.7	41.3	15.0	11.4	3.6
WS	121	292	1009	31.4	45.6	16.7	11.9	**4.8**
BG	78	120	788	37.0	27.0	9.1	8.1	1.0

synthetic production. The outlet exhausts of the flue gas and CO_2 emission have been lowered into the atmosphere by 0.164 10^6 and 0.084 10^6 t/a. The hydrogen and processed water coproduced the amounts of 4.6 10^3 t/a and 0.145 10^6 t/a.

This study could be ensured as environmentally sustainable for the commercial synthetic gasoline production, because the raw materials will be coming from the garbage as useless MSW and flue gas. The feasibility of this project could be made more feasible because of the usage of the existing available process units. The existing methanol process could be replaced with the synthetic gasoline production, because of increasing market demand. In this case the synthetic gasoline production would be a potential challenge for replacing the non-renewable petroleum. The long-term realisation view of the synthetic gasoline production is justified by using the multiple's effect technique because of the environmental and economic aspects. The potential operation and environmental uncertainties of the synthetic gasoline production were low because of the usage real model. The multiple's effect technique has simplified the calculation greatly and defined the optimal production of biogas from sorted MSW quickly. New research aims to clean the flue gases after gasification and return them to the process by using the pressure swing adsorption (PSA) columns with zeolites.

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Povzetek

Predstavljena je metoda večkratnega učinka, ki temelji na uplinjanju in ponovni uporabi trdnih komunalnih odpadkov (TKO) ter vključuje osnovni parameter večkratnega učinka (MU_W; $MU_{WNS} = 0$; $MU_{WPS} = 1$; $MU_{WS} = 2$), ki predstavlja stopnjo sortiranja od ne sortiranih do sortiranih TKO. Zaradi tega parametra in uporabe simulatorja Aspen Plus® se matematični model poenostavi za iskanje optimalne trajnostne surovine za proizvodnjo sinteznega plina, ki nadomešča netrajnosti zemeljski plin za nadaljnjo proizvodnjo metanola. Metodo smo testirali na obstoječem procesu in najboljša alternativa so sortirani TKO, s katerimi tudi proizvedemo največ metanola.

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