Simulation of the Conversion of Japanese Waste Biomass to Light Olefins: Reducing Biogenic Emissions via CO_2 Recirculation in the Water Gas Shift Reactor

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The significant availability of agricultural and forest residues in Japan impedes the traditional conversion through biochemical routes. In contrast to cellulose, lignin has a stronger chemical structure difficult to be decomposed via enzymatic or bacterial pathways. Thus lignified biomass waste can be easily converted through thermochemical degradation, as the aromatic structures of lignin can be break down with temperature between 550 - 900 °C. While biomass for energy utilization may induce negative environmental effects, the production of biomass-based chemicals promotes an added-value approach, avoiding combustion and the production of biogenic CO_2. Industrially available technologies enclose the conversion via gasification, methanol synthesis, and methanol to olefins. Unfortunately, this conversion pathway is also subject to CO_2 emissions during the gasification and the gas conditioning using water gas shift - WGS reactors. This study aims to assess the recirculation of the CO_2 produced in the WGS reactor while increasing the production of olefins and the process performance. This evaluation is performed with a dynamic process simulation in AVEVA™ PRO/II™. Preliminary results suggest a production of 200 kg of light olefins per ton of biomass, of while recycling CO_2 through the WGS reactor and capturing almost 70 % of the CO_2 emissions. The present study advises for further studies an extensive assessment of the WGS reactor operating conditions.

1. Introduction

In the petrochemical industry, light olefins (ethene, propene, and besides other alkanes) are the main building blocks to produce several daily life plastics. For this reason, light olefins are under revision for renewable feedstock and a more sustainable production (Talero and Kansha, 2022). Coincidentally, biomass has been pointed as a renewable source for substituting fossils, disclosing a positive life cycle to mitigate steam-cracking petrochemicals by producing bioplastics (i.e. polyethylene, polypropylene, or solvents) through biomass-derived ethylene or propylene (Ren et al., 2020). Lignified biomass also presents a high content of aromatic structures as pyrolytic lignin, easily converted to benzene, toluene and xylene – BTX, to produce nylon, PET fibers, or resin films. From all the variety of Japanese biomass, solid bio-waste is of main potential and lignified bio-waste pinpoints wood leftover and forest thinning, carboard, or rice straw and husk (Talero et al., 2021). Former revisions for Japan projected a hypothetical replacement of 21 % of petrochemicals with biomass-based feedstock. The significant availability of forest and agricultural residues in Japan hampers the traditional conversion through biochemical routes like anaerobic digestion, fermentation, or composting. (Kartal and Özveren, 2021). Still, biomass to olefins – BTO via thermochemical conversion continues on a conceptual design and the most promising industrial technologies on time enclose gasification, besides catalytic reactions like methanol synthesis, and methanol to olefins – MTO.

Despite the conversion pathway from BTO, oxygen and hydrogen contents are the main concerns in the atomic balance of the process (Jiang et al., 2019). While biomass normally contains over 40 % of oxygen in mass fraction, light olefins are double-bonded hydrocarbons free of oxygen. Hence, BTO is a conversion process that encompasses the removal of oxygen by producing typically H_2O and CO_2 in the reaction mechanisms. H_2O is more likely to be a recyclable molecule in the BTO conversion, particularly when using steam gasification. Unfortunately, this conversion pathway is also subject to CO_2 emissions during the gasification, conditioning,

and heat supply process. Although biomass for energy utilization may induce negative environmental effects, the production of biomass-based chemicals promotes an added-value approach. By avoiding combustion of biomass or biofuels, no CO_2 is released to the atmosphere but remains captured in daily goods as biochemicals, mitigating the biogenic CO_2 (Yadav et al., 2020). At first, the thermochemical conversion involves a set of endothermic reactions above 800 °C, resulting in a heat demand normally supplied with direct or indirect combustion. Likewise, most CO_2 emissions during the gasification reactions are favored because of the equilibrium between the water to gas primary reaction and the Boudouard reaction.
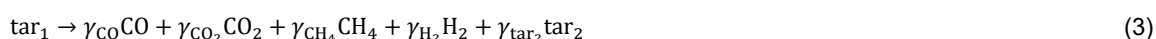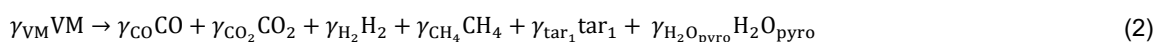
Finally, the conditioning of the so-called synthesis gas—syngas using water gas shift - WGS reactors, adjusts the ratio of H_2 to CO by modifying the content of CO_2 or H_2O, promoting the direct or reverse water to gas shift reaction.(Ribeiro et al., 2012). This conditioning is especially relevant for the methanol synthesis that abides by the stoichiometric molar ratio (H_2–CO_2)/(CO+CO_2) of the supply flow as close as 2.1 to maximize the methanol yield. The technical literature reported several strategies to adjust the H_2 to CO ratio in the feed syngas by modifying the gasifier operating conditions or recirculating syngas. For the former adjustment method, CO_2-riched syngas can be recirculated to the gasifier or redirected to the conditioning reactors like the WGS reactor. The recirculation of CO_2 to the gasifier is of interest in increasing the CO content in the syngas while increasing the char conversion. Still, this approach is limited to the slow heterogeneous reaction in the gasifier, the amount of char to react as a catalyst, or the dimensions of the reactor to promote a gas homogeneous WGS reaction. The conversion of CO_2 into CO within the syngas conditioning section is more likely faster and more flexible.

The main purpose of this study is to evaluate the effect of recirculating CO_2 through the WGS reactor on the production of methanol and further light olefins. This evaluation is done with a numerical simulation of the process in PRO/II™ and a layout design reported in the literature that includes steam gasification, syngas conditioning, methanol synthesis, and further methanol to olefins - MTO. The feedstock to be used in this study is a mix of woody biomass available in Japan in coherence with the thermochemical characterization of the former publication of the authors (Talero and Kansha, 2022). The used methodology follows an initial validation of the BTO model, then the accountability of the main system inflows and outflows to dimension CO_2 gross emissions, and a final revision of the effect of CO_2 recirculation in the BTO performance.

2. Thermochemical conversion of biomass to light olefins

2.1 Reaction mechanism

This BTO system is based on the previous process design reported in literature (Jiang et al., 2019). The initial stage of the process consists of the gasification that includes the pyrolysis of biomass, summarized in the Eq(1) and Eq(2). Biomass – BM is composed of only carbon, hydrogen, and oxygen. The fixed carbon – FC is only composed of carbon, while the volatile matter – VM contains the difference between BM and FC. The mass fractions of FV and VM are assumed as 16 % and 84 % (Talero and Kansha, 2022). Likewise, the tar cracking reaction of Eq(3), and the steam gasification zone that includes a set of reduction reactions at temperatures above 600 °C, both heterogeneous and homogeneous. The tar composition and reactions are taken from a former study of the authors (Talero and Kansha, 2022). The heterogeneous reactions are the Boudouard and the Water Gas primary reactions, according to Eq(4) and Eq(5).

$$BM_{daf} \rightarrow \gamma_{FC}FC + \gamma_{VM}VM \tag{1}$$

$$\gamma_{VM}VM \rightarrow \gamma_{CO}CO + \gamma_{CO_2}CO_2 + \gamma_{H_2}H_2 + \gamma_{CH_4}CH_4 + \gamma_{tar_1}tar_1 + \gamma_{H_2O_{pyro}}H_2O_{pyro} \tag{2}$$

$$tar_1 \rightarrow \gamma_{CO}CO + \gamma_{CO_2}CO_2 + \gamma_{CH_4}CH_4 + \gamma_{H_2}H_2 + \gamma_{tar_2}tar_2 \tag{3}$$

$$C + CO_2 \rightarrow 2CO \tag{4}$$

$$C + H_2O \rightarrow CO + H_2 \tag{5}$$

The homogeneous reduction include the reaction of unreacted pyrolysis gas, desorption gas, and the water steam, in a according to the WGS reaction of Eq(6). The gas cleaning and conditioning uses the same stoichiometric definitions of Eq(3) for tar reforming and Eq(6) for the WGS reactor. Conditioned syngas is then transformed into methanol with the global stoichiometric reaction as shown in Eq(7), in parallel with the WGS reaction of Eq(6), to convert part of the CO_2 into CO and water. The produced methanol is supposed to react under catalytic conditions with Zeolite SAPO-34 catalyst to produce initially DME and water, as presented in Eq(8). The DME sequentially reacts under catalytic conditions of Eq(9) to produce the list of light olefins ethylene, propylene, butene and pentane. No isomers are considered in the reaction mechanism or the list of products.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{6}$$

$$CO + 2H_2 \rightarrow CH_3OH \tag{7}$$

$$2\,CH_3OH \rightarrow CH_3OCH_3 + H_2O \tag{8}$$

$$n\,CH_3OCH_3 \rightarrow 2\,C_nH_{2n} + n\,H_2O \tag{9}$$

2.2 Model development

Figure 1 presents the flow-sheet topology for the conversion of BTO. The section on gasification is adapted from a former study by the authors (Talero and Kansha, 2022). In the present study, biomass is assumed to be Japanese forest residues with thermochemical properties reported in a former study by the authors. The simulation is evaluated at the constant temperature of 850 °C and S/B of 2 during gasification. The crude syngas comprises tar and the raw composition of the syngas and is cleaned and conditioned in the reformer reactor, scrubber, WGS reactor, and PSA. In the last stage of the conditioning, 10 % is maximum molar content of CO_2 in the cleaned syngas for the synthesis of methanol. The leftover CO_2 is recirculated through the WGS rector - the $CO_{2,rec}$ to react again at 400 °C and a steam-in of water as 3.03 ton/h. The un-reacted CO_2 is released to the atmosphere as $CO_{2,air}$, and varied during the case study. The CO_2 recirculation ratio is defined according to Eq(10) and is evaluated from 0 to 99.5 %.

$$CO_2\ recirculation\ ratio = \frac{\dot{m}_{CO_{2,rec}}}{\dot{m}_{CO_{2,air}} + \dot{m}_{CO_{2,rec}}} \tag{10}$$

After the syngas cleaning and conditioning, the synthesis of methanol is run at 10 MPa and 200 °C (Jasper and El-Halwagi, 2015). The recirculation of unreacted syngas after the methanol synthesis is not included in the present study for simplification. The produced methanol is directed to the MTO process, including an initial conversion to dimethyl ether - DME at 5 MPa and 150 °C. A former conversion of DME to olefins – C_nH_{2n} is simulated at 120 kPa and 500 °C. The model includes mass integration as the chemical revision only implies mass balance. Still, a further revision is planned for the energy integration, heat exchanger network, and power generation systems. The composition of the syngas is recorded before and after the reactor of methanol synthesis. The last section of the model converts the produced methanol to DME and a former reaction to light olefins considered ethylene, propylene, butene and pentane.
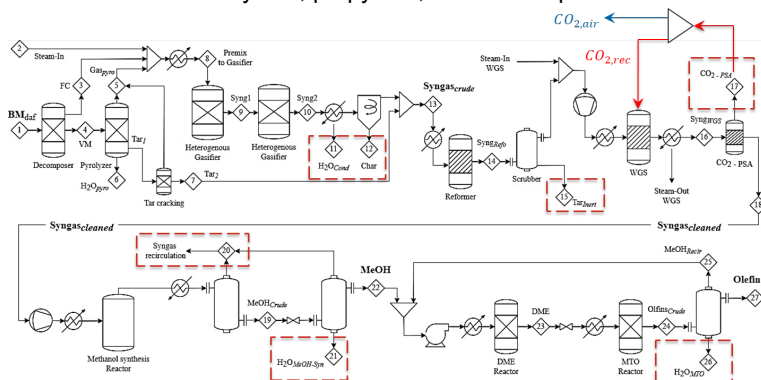

Figure 1: Flowsheet topology for the biomass to olefins via thermochemical conversion

Some simplifications are considered for the formulation of the simulation to size the constraints of unspecified data, limits of the software, and computing requirements (Talero and Kansha, 2022). The downdraft gasifier, gas conditioning, methanol synthesis, and MTO are constructed for a throughput of 10 ton/h of biomass, rebuilding the design of literature (Jiang et al., 2019). Steady-state and dimensionless conditions are assumed for the simulation to attain an isothermal process for all reactors. The biomass is supposed to be dry and free of ash. The simulation is implemented in AVEVA™ PRO/II™ Simulation 2020, a dynamic process simulator from Schneider Electric. "Peng Robinson" is used as the thermodynamic method to estimate the properties for non-polar materials with phase change. Peng Robinson is preferred over other thermodynamic methos for the stability and accuracy for a wide range hydrocarbons like alcohols, olefins or DME. Conventional compounds include H_2O, CO, CO_2, H_2, CH_4, and char. Non-conventional compounds include BM, VM, FC, and tar.

3. Simulation results

3.1 Validation of the model

The validation of the model employs experimental information of former studies (Zhang et al., 2009). The steam gasification model is based on a kinetic reaction model previously reported by the authors and validated for Woody biomass steam gasification (Talero and Kansha, 2022). The WGS reactor uses an equilibrium model that is based on extensive experimental data for the conversion of CO_2 to CO and H_2 (Graaf and Winkelman, 2016). For the methanol synthesis model, this study compares numerical results against experimental data reported in the literature for the operation of an industrial-scale methanol plant of Shiraz Petrochemical Company (Samimi et al., 2017). Table 1 presents a summary of the validation of the simulation result with The routine used in the current study allows the predictions of the listed light olefins with an absolute error of 1.8 % in the molar fraction of the composition of olefins.experimental data for Methanol synthesis, reporting a mean absolute error below 0.2 % in the methanol mass yield prediction. The MTO model is validated with experimental data reported in literature (Yao et al., 2021), using laboratory scale apparatus and SAPO-34 zeolites as a catalyzer, under reaction conditions of 400 °C, atmospheric pressure, and 0.5 g of catalyst. The model corresponds with experimental data to predict light olefins that include ethylene, propylene, and butane as major products with sensitivity above 96.9 %.

Table 1: Validation of the simulation for Methanol synthesis with experimental data reported in (Zhang et al., 2009). *AE is the absolute error between the model and the experimental mass yield.*

Reactor conditions	Model mass yield kg/h	Model mass yield % g/g	Exp. mass yield kg/h	Exp. mass yield % g/g	AE mass yield % g/g
T = 250 °C, P = 5 MPa, Inlet flow = 27 kg/h Syngas (% m/m): H_2 = 35.17 %, CO = 11.27 %, CO_2 = 8.32 %, CH_4 = 0.95 %, N_2 = 44.29 %	0.83	3.03 %	0.82	3.01 %	0.02 %
T = 255 °C, P = 6.67 MPa, Inlet flow = 64 ton/h Syngas (% m/m): H_2 = 76.07 %, CO = 6.06 %, CO_2 = 8.53 %, CH_4 = 4.3 %, N_2 = 4.58 %	11824	18.36 %	11283	17.52 %	0.84 %

3.2 Overall mass balance of the process

A summary of the main sub-systems inflows and outflows is presented in Table 2, evaluated without CO_2 recirculation and under local extreme conditions, named Max and Min. The last table excludes the intermediate flows of Syngas, methanol or DME, and allowing to measure the demand and availability of chemical during the process. The conditions of simulation that present maximum flows – Max, are evaluated at S/B of 3, and gasification temperature of 850 °C. Likewise, minimum flow – Min is simulated at S/B of 0 and temperature of 850 °C during gasification. The last revision reveals a maximum water recovery of the system above 98 %, ignoring possible problems and challenges of reusing tar-contaminated water or energy consumption during water purification and cleaning. Burnable steams include inert tar and un-reacted char produced during the gasification, as the tail gas, un-reacted syngas (syng-rec), and un-reacted methanol during the methanol synthesis and MTO. It is possible to estimate a heat generation of the burnable steam near 4.4 MW with a potential of electric power generation near 0.8 MW. The CO_2 emissions are mainly released during the PSA separation in the syngas cleaning section, with a smaller fraction in the Methanol synthesis tail-gas. The CO_2 outflow highly depends on the S/B operating conditions during the gasification, at fixed parameters of the WGS reactor, methanol synthesis, or MTO.

3.3 Effect of CO_2 recirculation

Figure 2(a) presents the amount of CO_2 released into the atmosphere as a function of the CO_2 recirculation ratio of Eq(10). A raise in CO_2 recirculation reduces the amount of biogenic CO_2 in the process. Unfortunately, this recirculation also increases the flow of CO_2 within the system as a fraction of the biomass inflow - $\dot{m}_{CO_{2,rec}}/\dot{m}_{BM_{daf}}$. The increment of the CO_2 recirculation has a direct influence on the dimensions of the WGS reactor up to 8 times the size of the reactor to achieve a CO_2 recirculation ratio above 98 %. These design conditions can be undesirable for a balanced economical design. Out of a fluctuating and temporary subsidized carbon credit market, there are no stable and direct economic benefits for a complete mitigation of CO_2 emissions. A closer evaluation of the performance of the process is presented in Figure 2(b), by reporting the effect of CO_2 recirculation on the yield of products. While the amount of syngas produced is increasing in high recirculation scenarios, the amount of CO_2 contained in the syngas hinders the production of methanol. As a result, the methanol and further olefins yield expose local maximum values with a recirculation of CO_2 per

biomass mass - $\dot{m}_{CO_2,rec}/\dot{m}_{BM_{daf}}$ near 1.5 g/g$_{BM}$. The last operating conditions suggest a CO$_2$ recirculation ratio of 0.7, achieving a reduction of the CO$_2$ biogenic emissions from 10.9 ton/h without CO$_2$ recirculation, to 3.2 ton/h of CO$_2$ to the atmosphere. A closer revision of the un-reacted syngas after the methanol synthesis is presented in Figure 3(a). Variations of the H$_2$ present in the un-reacted syngas suggest that after $\dot{m}_{CO_2,rec}/\dot{m}_{BM_{daf}}$ of 1.5 g/g$_{BM}$, the WGS reactor lacks hydrogen to produce methanol. Indeed, the stoichiometric ratio of H$_2$ to CO is below 2.1 after $\dot{m}_{CO_2,rec}/\dot{m}_{BM_{daf}}$ of 1.5 g/g$_{BM}$.

Table 2: Mass balance of main by-products in the conversion of biomass to olefins, under minimum conditions – Min and maximum conditions Max

Section	Mass Steam IN	Min ton/h	Max ton/h	Mass Steam OUT	Min ton/h	Max ton/h
Gasification	BM	10.0	10.0	H$_2$O-PYRO	1.13	1.13
	STEAM IN	0	30	H$_2$O-COND	22.16	29.05
Syngas cleaning	STEAM-IN-WGS	3.03	6.81	TAR-INERT	0.13	0.14
				STEAM-OUT	1.78	2.84
				CO$_2$-PSA	3.10	10.65
MeOH synthesis				SYNG-REC	1.09	2.75
				H$_2$O-MeOH-Syng	0.22	1.00
MTO				H$_2$O-MTO	1.49	3.18
				MeOH-UNREAC	0.17	0.37
Summary	IN	Min ton/h	Max ton/h	OUT	Min ton/h	Max ton/h
	Total water	3.03	36.81	Total water	26.80	37.20
	Total CO$_2$	0	0	Total CO$_2$	3.21	10.93
	Total burnable	0	0	Total burnable	1.34	4.56

The amount of CO increases rapidly after a H$_2$ to CO ratio above 2.1, due to the lack of hydrogen to produce methanol. As a result, the adjustment of the H$_2$ to CO ratio during the synthesis of methanol seems to be the most predominant performance variable of the process (Puig-Gamero et al., 2018). Thus, Figure 3(b) exposes the influence of the olefin yield not only by the CO$_2$ recirculation but also by the gasification conditions as the S/B or gasification temperature.
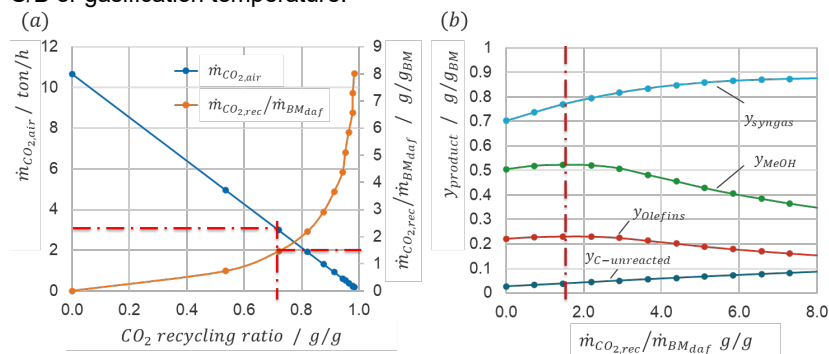

Figure 2: Effect of the recirculation of CO$_2$ and S/B in, (a) biogenic CO2 evolved; and (b) yield of product distribution
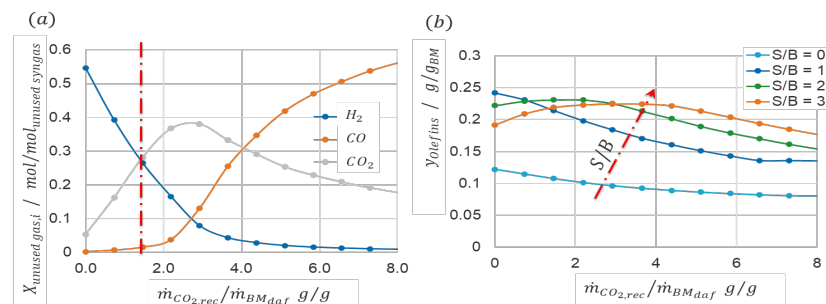

Figure 3: Effect of recirculation of CO$_2$ in (a) unreacted syngas after methanol synthesis; and (b) olefins yield and products distribution.

4. Conclusions

The evaluation of the CO$_2$ recirculation through the WGS reactor suggest a reduction of biogenic CO$_2$ while affecting the yields of methanol and light olefins without a linear trend. The current study pinpoints a relevant influence of the syngas cleaning and conditioning to maximize the BTO performance. Indeed, the syngas composition to feed the methanol synthesis maximizes the yield of methanol when the stoichiometric ratio of H$_2$ to CO is close to 2 mol/mol. The simulation results indicate a possible mitigation of 70 % of the CO$_2$ biogenic emissions enabling the production of near to 200 kg light olefins per ton of woody biomass – daf. The last scenario can be carried out with a temperature of 850 °C during gasification, S/B of 2, and operating the WGS reactor at 400 °C and a steam-in of water as 3.03 ton/h. Still, the last conditions can be achieved not only by adjusting the CO$_2$ recirculation ratio, but also modifying the gasification conditions. An extensive revision of the gasification conditions is advised for future studies.

Nomenclature

ad – as determined basis
BTO – Biomass to olefins
S/B – mass ratio of steam to biomass
daf – basis dry and free of ash
X_i – molar fraction of component i

AE – absolute error
rec – subindex for recirculation
$Syng$ – subindex for syngas
MeOH – Methanol
$y_{product}$ – mass yield of product

References

Graaf G.H., Winkelman J.G.M., 2016, Chemical equilibria in methanol synthesis including the water-gas shift reaction: A critical reassessment, Industrial and Engineering Chemistry Research, 55(20), 5854–5864.

Jasper S., El-Halwagi M.M., 2015, A techno-economic comparison between two methanol-to-propylene processes, Processes, 3(3), 684–698.

Jiang P., Parvez A.M., Meng Y., Xu M.X., Shui T.C., 2019, Exergetic, economic and carbon emission studies of bio-olefin production via indirect steam gasification process, Energy, 187, 115933.

Kartal F., Özveren U., 2021, A comparative study for biomass gasification in bubbling bed gasifier using Aspen HYSYS, Bioresource Technology Reports, 13, 100615.

Puig-Gamero M., Argudo-Santamaria J., Valverde J.L., Sánchez P., Sanchez-Silva L., 2018, Three integrated process simulation using aspen plus®: Pine gasification, syngas cleaning and methanol synthesis, Energy Conversion and Management, 177, 416–427.

Ren X.Y., Feng X.B., Cao J.P., Tang W., Wang Z.H., Yang Z., Zhao J.P., Zhang L.Y., Wang Y.J.Y., Zhao X.Y., 2020, Catalytic conversion of coal and biomass volatiles: A review, Energy Fuels, 34, 10307–10363.

Ribeiro A.M., Santos J.C., Rodrigues A.E., Rifflart S., 2012, Syngas stoichiometric adjustment for methanol production and co-capture of carbon dioxide by pressure swing adsorption, Separation Science and Technology, 47 (6), 850–866.

Samimi F., Rahimpour M.R., Shariati A., 2017, Development of an efficient methanol production process for direct CO$_2$ hydrogenation over a Cu/ZnO/Al$_2$O$_3$ catalyst, Catalysts, 7(11), 332.

Talero G., Kansha Y., 2022, Simulation of the steam gasification of Japanese waste wood in an indirectly heated downdraft reactor Using PRO/II™: Numerical comparison of stoichiometric and kinetic models, Energies, 15(12), 4148.

Talero G., Nielsen C.M., Kansha Y., 2021, Identification of Japanese solid biowaste for conversion into biochemicals and energy via thermochemical biorefinery, Chemical Engineering Transactions, 88 , 313–318.

Yadav V.G., Yadav G.D., Patankar S.C., 2020, The production of fuels and chemicals in the new world: Critical analysis of the choice between crude oil and biomass vis-à-vis sustainability and the environment, Clean Technologies and Environmental Policy, 22(9), 1757–1774.

Yao J., Tian H., Zha F., Ma S., Tang X., Chang Y., Guo X., 2021, Regulating the size and acidity of SAPO-34 zeolites using dual templates to enhance the selectivity of light olefins in MTO, New Journal of Chemistry, 45(26), 11812–11822.

Zhang Y.N., Xiao J., Shen L.H., 2009, Simulation of methanol production via rice straw gasification in interconnected fluidized beds, Zhongguo Dianji Gongcheng Xuebao/Proceedings of the Chinese Society of Electrical Engineering, 29(32), 103–111.