Developing a simulation model for a mixed alcohol synthesis reactor and validation of experimental data in IPSE~pro~

G. Weber [a],*, A. Di Giuliano [a], R. Rauch [a], H. Hofbauer [b]

[a] Bioenergy 2020 + GmbH, Wiener Straße 49, 7540 Güssing, Austria
[b] Vienna University of Technology, Institute of Chemical Engineering, Getreidemarkt 9, 1060 Vienna, Austria

A B S T R A C T

The production of higher alcohols over a sulfidized molybdenum catalyst (MoS_2) using a biomass-derived synthesis gas has been studied at Güssing for several years. The mixed alcohol (MA) pilot plant uses synthesis gas provided by the biomass-based combined heat and power plant (CHP) Güssing. Parameter variations were carried out wherein temperature, space velocity and gas composition were varied to evaluate the impact on CO conversion, product distribution and yield. The influence of side reactions to hydrocarbons was also a research objective. A sufficient amount of experimental data was obtained during these experiments. Evidence for the influence of various reaction parameters was found, but the mass balance could not be closed. A mathematical model of the MA synthesis reactor was developed using the stationary equation-orientated flow sheet simulation software IPSE~pro~. This publication gives an overview of modeling the MA reactor and condenser unit and testing the model with example calculations. Validated experimental results from 2012 parameter variation are shown and a comparison between experimental and validated quantities is carried out. A comparison with literature data shows that the observed tendencies are in good correlation to literature. The developed reactor model was enabling the possibility for carrying out a validation of the experimental data. IPSE~pro~ uses the method of least-squares to obtain the approximate solution of the overall determined system. The established model was very close to the actual MA pilot plant. The model is very accurate about MA liquid product compositions and all measured flows.

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1. Introduction

Increasing demand for fuel as well as the depletion of oil resources has created interest in alternative fuel sources. A promising route for the production of high quality fuels and chemicals is the gasification of biomass and the synthesis of hydrocarbon compounds like Fischer–Tropsch (FT), DME (Dimethylester), methanol, ethanol and MA synthesis. The thermochemical pathway over gasification and chemical synthesis has, in comparison to fermentation technologies, the ability to convert a wide variety of biomass feed stocks into usable products. Second-generation biofuels are generated by this technology route, which has the advantage that the provided fuels are not in competition with the food industry like first generation biofuels. MA synthesis is an interesting route for the production of a bioblending component for gasoline with a high octane number [1,2]. MAs are defined as a blend of alcohols with carbon numbers in the range of one to five. The advantages of MAs are a better octane number, reduced toxic exhaust gas, lower

Reid vapor pressure, higher energy content and better miscibility in gasoline versus other fuels like pure methanol or ethanol. Besides their use as blending components for gasoline, they can also be used in the chemical industry as a base material [3].

The possibility of producing methanol and other alcohols over an alkali doped Zn- and Cu-based catalyst at a certain temperature and pressure has been well known since the 1920s. Co- and Fe-based catalysts for the production of mainly non-oxygenated hydrocarbons (FT products) diverted attention away from the production of synthetic alcohols. No commercial plants for MA synthesis exist today, but it is still an interesting field of research with great future potential [4].

The research is now more focused on MA synthesis with alkali-doped molybdenum sulfide (ADMS) catalysts, because it seems to be the most economically promising catalyst. The main advantage is the resistance to sulfur, which reduces the investment costs in such a plant tremendously. The chemistry of MA synthesis on the basis of an ADMS catalyst is complicated. Besides the formation of MA, several side reactions occur (FT synthesis of paraffins and olefins, WGS, ester formation). The produced MA and paraffins, respectively, follow an ASF distribution. An ADMS catalyst is also used in the Güssing pilot plant.

The main focus of experiments with the pilot plant was to carry out parameter variations of temperature, pressure, gas composition and

* Corresponding author.
  E-mail addresses: gerald.weber@bioenergy2020.eu (G. Weber),
andrea.digiuliano@graduate.univaq.it (A. Di Giuliano), reinhard.rauch@bioenergy2020.eu
(R. Rauch), hermann.hofbauer@tuwien.ac.at (H. Hofbauer).

space velocity to yield sufficient experimental data to disclose the mass balance of the plant and select the proper plant setup and reaction conditions for a plant on a demonstration scale. During parameter variation a sufficient amount of raw experimental data was generated. The closing of the mass balance using raw experimental data was not possible. A mathematical model of the MA synthesis reactor and product separation using a "black-box" model approach was developed with the simulation tool IPSE$_{pro}$. The developed simulation model was further used for validation of the experimental data. This paper gives an overview of modeling the MA reactor and condenser unit and testing the model with example calculations. Validated experimental results from 2012 parameter variation are shown and a comparison between experimental and validated quantities is carried out. A comparison with literature data shows that the observed tendencies are in good correlation to literature.

2. Material and methods

2.1. CHP plant Güssing

A dual fluidized bed (DFB) steam gasification system is used in Güssing to produce a high quality synthesis gas. Fig. 1 shows the functionality of the DFB steam gasification system as an allothermic gasification process with an external heat input.

In principle, a bubbling fluidized bed gasification reactor, which is fluidized with steam, is coupled with a circulating fluidized bed combustion reactor that is fluidized with preheated air. The bed material and non-gasified carbon are transported from the gasification zone through a chute into the combustion zone. The bed material is heated up in the combustion zone and separated from the flue gas by a cyclone. The separated bed material transfers the heat in the gasification zone. The bed material covers the energy demand for the strongly endothermic gasification process. In the gasification zone the biomass is converted at temperatures of 1123 K to 1173 K over the main steps heating up, drying and devolatilization, mainly into H_2, CO, CO_2, CH_4, H_2O (gas) and C (char). Small amounts of by-products like C_2H_4, C_2H_6 and undesirable components like tar, NH_3 and H_2S are also produced. The synthesis gas is further cooled to 433 K–453 K with a water cooled heat exchanger, particles and tar are separated with a fabric filter, and residual tars and the water are removed with a scrubber using RME (rapeseed methyl ester) as solvent. In the gas scrubber, the product gas is cooled to approximately 313 K. The scrubber also lowers the amount of water by 50 to 10 vol.% [5,6]. The cleaned synthesis gas can then be used for the production of heat and power in a gas engine or for gas synthesis applications like the production of FT, H_2 or MAs. In Table 1, the gas composition of the cleaned synthesis gas with water content of about 10 vol.% is shown [6].

2.2. Mixed alcohol synthesis

MA synthesis is an exothermic chain propagation reaction. The stoichiometry and exothermic nature of the reaction dictate that the
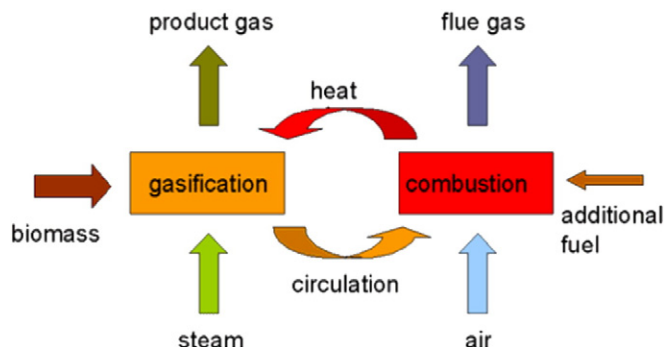

**Fig. 1.** Principle of the DFB gasification system [5].

Table 1
Gas composition of CHP plant Güssing (dry) [6].

| *Main components*		
Hydrogen	35–45	vol.%$_{dry}$
Carbon monoxide	19–23	vol.%$_{dry}$
Carbon dioxide	20–25	vol.%$_{dry}$
Methane	9–11	vol.%$_{dry}$
Minor components		
C_2H_4	2–3	vol.%$_{dry}$
C_2H_6	~0.5	vol.%$_{dry}$
C_3H_8	~0.5	vol.%$_{dry}$
O_2	<0.1	vol.%$_{dry}$
N_2	~1	vol.%$_{dry}$
Particles	30–100 (after gasifier)	g/Nm^3
Tars	1–5 (after gasifier)	g/Nm^3
BTX	~10	g/Nm^3
Catalyst poisons		
H_2S	~150	ppm$_v$
COS	~5	ppm$_v$
Mercaptans	~30	ppm$_v$
Thiophenes	~7	ppm$_v$
HCl	~3	ppm$_v$
NH_3	500–1500	ppm$_v$
HCN	~100	ppm$_v$

catalyst should be operated at low temperatures and high pressures. The main reaction is the formation of alcohols. Possible side reactions are the formation of hydrocarbons and the water gas shift reaction [7].

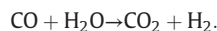The following reactions can occur [7,8]:

- Formation of alcohols:

$$nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O$$

- Formation of hydrocarbons:

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$
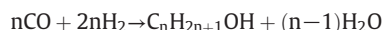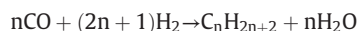
- Water gas shift (WGS) reaction:

$$CO + H_2O \rightarrow CO_2 + H_2.$$

Hydrogenation, the breaking of C–O bonds and CO insertion all take place over MA synthesis catalyst. An acyl intermediate is formed over the CO insertion into a metal-alkyl bond. The hydrogenation of the acyl intermediate can form an alcohol molecule. The formed intermediates are dependent mainly on the type of catalyst used in the composition, structure and reaction conditions. The formation of intermediates and their further reaction are influenced by the active metals used, the preparation formula and the process conditions [7].

Heterogeneous catalysts for the synthesis of ethanol and higher alcohols can be classified into two main categories [7,4]:

Noble metal-based catalysts:

- Primarily supported Rh catalysts, which produce mainly ethanol and other C_2-oxygenates

Non-noble metal-based catalysts, which favor the formation of a spectrum of MAs with carbon numbers between one and six:

- Modified high pressure methanol synthesis catalysts such as alkali-doped ZnO/Cr_2O_3
- Modified low pressure methanol synthesis catalysts such as alkali-doped Cu/ZnO and $Cu/ZnO/Al_2O_3$
- Modified FT catalysts such as alkali-doped $CuO/CoO/Al_2O_3$
- Alkali-doped molybdenum sulfide (ADMS) catalysts.

The MA synthesis mechanism consists of a number of reaction pathways with miscellaneous routes to different products. Research ADMS

catalysts provided by our project partner Albemarle were used for the experiments with Güssing MA synthesis pilot installation. ADMS catalysts (using K as a dopant) form predominantly linear alcohols in an extremely complicated reaction system with several possible products. The CO insertion mechanism is a generally accepted mechanism for alcohol formation over Mo-based catalysts. The elementary steps of the MA synthesis reactions can be classified as initiation of chain growth, chain growth reactions and termination of chain growth. The mechanism starts with associative adsorption of CO and dissociative adsorption of H_2 on the catalytic active site. The methyl intermediate R_1O_s is formed by repeated hydrogenations by adsorbed H on adsorbed CO. The insertion of CO and its hydrogenation forms various adsorbed precursors of the final product (esters, alkanes, alkenes, methanol and other alcohols). The termination of chain growth is initiated with the hydrogenation of the precursors of the final products [8].

Maximum alcohol formation occurs between 593 K and 623 K [9,8, 3]. Temperature is one of the most critical parameters because it has a profound influence on the MA synthesis kinetics and their selectivity. CO conversion, the formation of CO_2 and the formation of paraffins increase with rising reaction temperature. Above a reaction temperature of 593 K–623 K, the FT reactions to paraffins, like CH_4 and C_2H_6 are significantly enlarged [8]. With an increase in the reaction pressure, CO conversion and the formation of CO_2 are increased [8]. The H_2/CO ratio mainly influences the product distribution. The formation of methanol and CH_4 is favored by H_2/CO ratios over two [8]. H_2/CO ratios less than one can deactivate the catalyst by coke formation [4]. With a decrease in space velocity the tendency to side reactions like the formation of hydrocarbons is increased [8].

2.3. MA synthesis pilot plant and experimental measures

Fig. 2 gives an overview about the plant setup and the online measurement points for important quantities.

The gas is taken before the gas engine, after the gas cleaning steps at the biomass CHP, so particles and heavy tars are already removed. A stable system pressure before the compressor is guaranteed by a product gas blower before the steam reformer. The pressure before the compressor is kept constant over the frequency controlled blower, which levels out the pressure drop over the reformer. Hydrocarbon compounds (CH_4, C_2H_6, C_2H_4 and aromatic compounds) are converted to H_2 and CO. The steam reformer also represents the main gas cleaning device in the plant setup. The reforming unit consists of two heat resistant stainless steel pipes. The gas is first heated up to around 773 K and

steam is added. The second pipe is the reactor pipe where the gas is heated further to around 1173 K and reforming reactions take place on the surface of a noble metal based catalyst. The gas is cooled below 373 K by an air cooled heat exchanger. Afterwards the gas is dried in a glycol scrubber. Nearly all the water from the synthesis gas is separated from the gas stream by cooling to about 275 K. A pressure of 9 to 30 MPa can be delivered by the compressor. The maximum flow is around 5 Nm^3/h. A bypass system is deployed for adjusting the volume flow over the MA synthesis plant. The MA synthesis reactor operates as a fixed bed reactor. The cleaned synthesis gas enters the reactor from the top and flows through the catalyst packed bed. The temperature range for this type of synthesis is in the range between 523 K and 623 K. The separation of the MAs from the gas stream is carried out by condensation in a cooled heat exchanger in the high pressure part of the plant. The separated alcohols are withdrawn over a needle valve into a collection vessel. The off-gas is expanded over an expansion valve to ambient pressure and sent back to the CHP plant.

Measured quantities at several points of the plant are:

- Temperatures (TIR)
- Pressures (PIR)
- Flows (FIR)
- Compositions (AR).

Temperature, pressure and flow are continuously measured and recorded during experiments. From examination of the main parameters it can be seen that a stable and stationary operating condition was reached. At stationary operating conditions the composition of the gas stream is determined by online measurements via gas chromatography (GC) using a GC Clarus 500 from Perkin Elmer. The GC is equipped with three different columns, i.e. two apolar and one 5 Å mole sieve, connected by two automated valves and a 500 µl injection loop. Helium is used as the carrier gas. Two types of detectors are used: a thermal conductivity detector (TCD) and a flame ionization detector (FID). The TCD is used to analyze the concentrations of permanent gases (O_2, CO, CO_2, and N_2). Hydrocarbons with carbon numbers up to three were analyzed using the FID detector. H_2 was calculated as 100 minus the sum of all other components given by both detectors.

The final MA condensed product composition is measured by GC as well, in this case not online but by taking several samples. The composition of the yielded alcohols was determined by gas chromatography using a GC Clarus 500 from Perkin Elmer. The alcohols were identified with a FID detector and a TCD detector was used to determine the
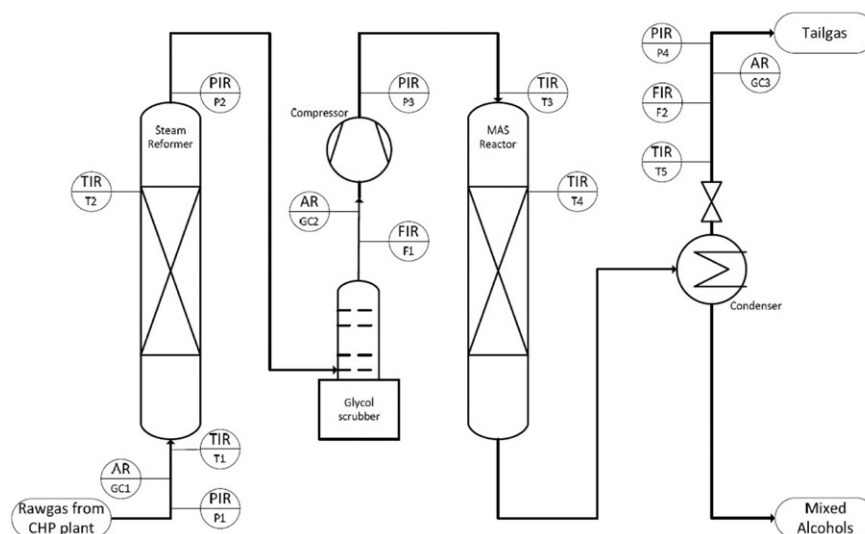

Fig. 2. MA synthesis pilot plant with online measurement points (TIR: temperature, PIR: pressure, FIR: flow, AR: composition).

quantity of water in the product. The flow of the MA final condensed product is not directly measured, but calculated by dividing its total mass by the operating time.

2.4. Introduction to IPSE_pro simulation software

2.4.1. Model development with MDK and flow sheet simulation with PSE

IPSE_pro is a stationary equation orientated flow sheet simulation software for the creation of process models and for utilizing these models throughout the lifecycle of a process plant, from conceptual design to online monitoring and optimization. Its main areas of application are energy engineering and chemical engineering [10].

Equation oriented means that the model equations together with the information from the flow sheet form a system of equations. These equations can be solved by numerical methods like the Newton–Raphson-Algorithm. The main advantage of an equation oriented approach is the rapid convergence of the system, with an average calculation time in only a few seconds. The stationary simulation tool allows the simulation of steady state operating points. Time dependent phases in an operating plant cannot be simulated [10].

Fig. 3 gives an overview of the fundamental system architecture of IPSE_pro. The MDK model package allows the creation and modification of models in an existing library or the creation of a new library [11]. The PSE unit represents the environment where the stationary process is simulated. The process can be created on the basis of objects from a library loaded by the user. Within the PSE no information is stored. The icons are chosen from the menu; they are placed properly and connect appropriately. The numerical data are entered and displayed in the same project window together with numerical calculation results. The imposed numerical data can be "set" at values identified by the user, while others are calculated by PSE as "estimates" [12].

The thermodynamic property data are typically not included in the actual simulation software, but are imported from external property libraries in the format of a dynamic link library (DLL). Needed new substances can be introduced by the user by creating an additional property-DLL [10].

The PSE Kernel uses a two-phase equation-oriented approach. In the first step PSE determines the best resolution path for the process in such a way that the variables are collected in groups. The number of variables should be minimized to find the best numerical calculation for each group. In the following step the numerical solution for each group is carried out with a Newton–Raphson-Algorithm based method [11,12].

IPSE_pro defines three classes of models [11]:

- Units: These are nodes in the network structure and represent actual pieces of equipment.
- Connections: These connect units in the network structure, representing the information that is transferred between two units (e.g. streams for mass flow, engine shafts for energy).
- Globals: These are information not directly sketched in the network structure but shared by an undefined number of objects (e.g. qualitative chemical compositions).

2.4.2. Validation of experimental data with PS Validate

The module PS Validate of the IPSE_pro program package applies the method of least-squares for data reconciliation. The process model is solved with a data adjustment algorithm that minimizes the weighted sum of the squares of the differences between redundant measured values and adjusted values, adhering to the conditions of respected process model equations. The great advantage of PS Validate is that the same process models developed in PSE can be used. The only difference is that some variables have to be defined as "measurements", thereby creating a redundancy within the process model. The process of reconciliation is applied on all variables stated as "measurements" [13].

The statistical assessment in PS Validate is the application of statistical tests on the just reconciled values [13].

PS Validate employs the "Lagrange multipliers method" to solve the data reconciliation problem. It is applied similarly to the standard PSE-Kernel solver in a two-step approach:

1) System analysis: the least square criterion is incorporated in the total equation system using Lagrange multipliers and thereby the problem becomes solvable. The equation system is analyzed and divided into groups as is done in PSE-Kernel.
2) Numerical solution: following the order established previously, a numerical solution is found.

The final calculation results for the reconciliation problem are shown in a calculation protocol.

PS Validate uses statistical considerations that require certain assumptions about the statistical significance of the data. The most common one is to consider variables as normally distributed. With this information it is possible to calculate the standard deviations of reconciled results using the law of error propagation, give confidence of reconciled intervals for the adjusted variables and consequently be able to identify and eliminate unreliable data [13].

Several statistical tests can be performed to verify the results' correctness at a chosen confidence level (usually 95%). If a test fails, either the quality of the data was overestimated or the process model doesn't adequately represent the real phenomenon.

3. Results and discussion

3.1. Modeling of MA synthesis in IPSE_pro

A model of the MA synthesis reactor and condenser had to be developed in order to obtain more reliable information about process performance in the sense of conversion rates, productivities and so on. The development of a detailed MA synthesis reactor model based on ADMS with integration of all possible side reactions and a thermodynamic and kinetic approach requires quite extensive development work. The final scope of the presented work was to establish a closed mass balance for MA synthesis in a stationary computer simulation in IPSE_pro. The application is not oriented to study the chemical behavior
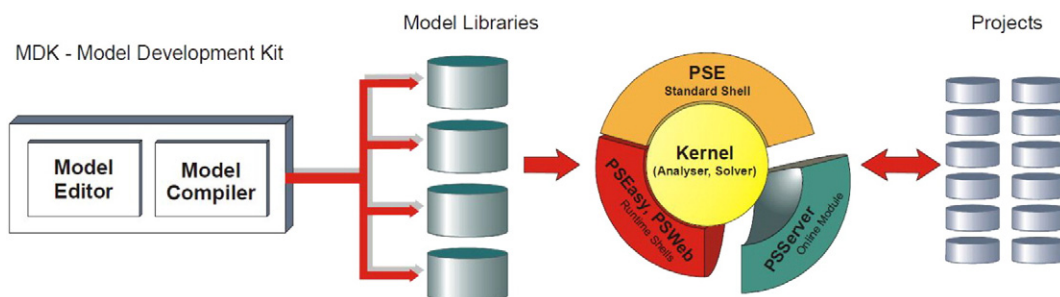

Fig. 3. System architecture IPSE_pro [11].

of a catalyst in detail, but to provide useful quantitative information in the context of economic feasibility or scale-up analysis.

Defining the most relevant chemical equations from the entire product pool of MA synthesis is substantial work for a simple model with short calculation time in PSE and shorter programming time in MDK.

It has been reported in the literature [7,8] and confirmed by Güssing's experimental results that within all classes of reaction for MA synthesis on ADMS the truly quantitatively relevant ones are:

- Alcohol formation,
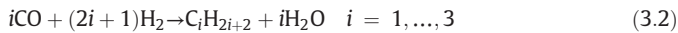- FT alkane formation
- WGS reaction.

The formation of esters and FT alkenes can be ignored. It is also known that because of the MA synthesis mechanism on ADMS, only linear alkanes and primary linear alcohols are produced [14,8]. Based on experimental results only alcohol and alkane carbon chain lengths from C1 to C3 need to be considered. It is known from the literature that alcohols and alkanes produced by MA synthesis on ADMS follow the ASF distribution [14,8]. 1-Propanol generated from Güssing's experiments shows a different behavior. The measured experimental concentrations of 1-propanol were always higher than predicted by the ASF distribution in accordance with methanol and ethanol. It has been shown that this higher propanol amount arises from a side reaction of C_2H_4 with CO and H_2 [15]. The presence of C_2H_4 in the syngas leads to the possibility of its hydrogenation to C_2H_6, which results in additional amounts of 1-propanol beyond what is calculated by ASF distribution of FT alkane formation.

Below the chemical reactions necessary in the MA synthesis model are obvious.

Primary linear alcohol formation [main reaction]:

$$i CO + 2i H_2 \rightarrow C_i H_{2i+1} OH + (i-1) H_2O \quad i = 1, ..., 3 \tag{3.1}$$
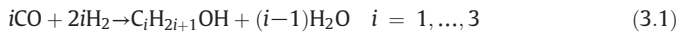
F–T alkane formation [side reaction]:

$$i CO + (2i+1) H_2 \rightarrow C_i H_{2i+2} + i H_2O \quad i = 1, ..., 3 \tag{3.2}$$

Ethylene to propanol [side reaction]:

$$C_2H_4 + CO + 2H_2 \rightarrow C_3H_7OH \tag{3.3}$$

Ethylene hydrogenation [side reaction]:

$$C_2H_4 + H_2 \rightarrow C_2H_6 \tag{3.4}$$

Water gas shift [side reaction]:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{3.5}$$

A "black-box" approach was used for modeling the MA synthesis reactor and condenser in a unique unit with compressed syngas as inlet, tailgas (with unreacted syngas and gaseous products) and condensed MA aqueous solution as outlets.

The black-box representing the MA synthesis reactor and condenser model assumes that the water and alcohols are flowing out of the reactor totally condensed and they constitute the MA synthesis liquid product. The unreacted syngas and side reaction products constitute the syngas. It is stated that alcohols and water are perfectly separated by condensation, while other species behave as permanent gases.

Fig. 4 shows the MA synthesis reactor and condenser in one unit object.

The performance of the MA synthesis is focused on CO conversion. CO is consumed in all reactions except C_2H_4 hydrogenation. The total CO conversion X_{CO} can be defined as a summation of the CO conversions in each one of these chemical paths (Eqs. (3.6) and (3.7)). For linear primary alcohol formation X_{CO}^a and FT paraffins X_{CO}^P a total CO conversion into alcohols or paraffins from C1 to C3 can be assumed because of the assumption of ASF distribution inside each class of products:

$$X_{CO} = X_{CO}^a + X_{CO}^P + X_{CO}^{\text{side propanol}} + X_{CO}^{\text{WGS}} \tag{3.6}$$

X_{CO} Total CO conversion [%]
X_{CO}^a Linear primary alcohol formation [%]
X_{CO}^P Linear FT paraffin formation [%]
$X_{CO}^{\text{side propanol}}$ Formation of side propanol [%]
X_{CO}^{WGS} CO consumption water gas shift reaction [%]

$$X_{CO}^k = \frac{CO_{\text{moles consumed in reaction "k"}}}{CO_{\text{moles fed to reactor}}} \left[\frac{\text{mol/h}}{\text{mol/h}}\right] \tag{3.7}$$

X_{CO}^k CO conversion in reaction k [%].

The ethylene hydrogenation also has to be considered. Because the hydrogenation of C_2H_4 is independent from the CO, the definition of another reference substance is necessary. C_2H_4 is the reference substance and its conversion in hydrogenation is:

$$X_{C_2H_4}^{\text{hydrogenation}} = \frac{C_2H_{4\,\text{moles consumed in hydrogenation}}}{C_2H_{4\,\text{moles fed to the reactor}}} \left[\frac{\text{mol/h}}{\text{mol/h}}\right]. \tag{3.8}$$

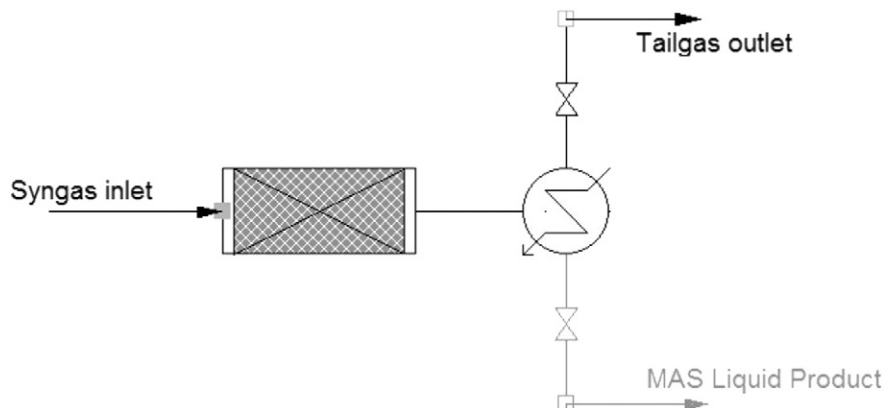$X_{C_2H_4}^{\text{hydrogenation}}$ Conversion of C_2H_4 in hydrogenation [%].

Fig. 4. PSE icon of MA synthesis reactor/condenser unit edited by MDK.

The production or consumption of moles of each substance is expressed as a function of CO conversion or C_2H_4 conversion in hydrogenation.

After the definition of all molar variations occurring in the reactor they can be used as "generative terms" to write stationary molar balances around the MA synthesis reactor/condenser unit object. A total mass balance around the unit and molar balances for all chemical species belonging to global objects, whose connection objects that cross the MA synthesis reactor/condenser unit refer to, is important to ensure the stability of the unit model in $IPSE_{pro}$ and to satisfy the mass conversion principle.

The disadvantage of the black-box modeling approach is the loss of details about energy fluxes. A global enthalpy balance in the closed MA synthesis reactor/condenser unit was established by defining an overall enthalpy difference. This approach provided an order of magnitude of relevant energy fluxes.

$$\Delta H_{overall} = F\,h(T) + F_{tailgas}h_{tailgas}(T_{tailgas}) - F_{syngas}h_{syngas}\,(T_{syngas}) \quad (3.9)$$

$\Delta H_{overall}$ Overall enthalpy variation across MA synthesis reactor/condenser unit [kW]
F Mass flow of MA synthesis liquid product [kg/s]
$h(T)$ Specific enthalpy of MA synthesis liquid product at T [kJ/kg]
$F_{tailgas}$ Mass flow of tailgas [kg/s]
$h_{tailgas}(T_{tailgas})$ Specific enthalpy of tailgas at $T_{tailgas}$ [kJ/kg]
F_{syngas} Mass flow synthesis gas [kg/s]
$h_{syngas}\,(T_{syngas})$ Specific enthalpy synthesis gas at T_{syngas} [kJ/kg].

It is assumed that tailgas and MA synthesis liquid product have the same temperature ($T_{tailgas} = T$). Furthermore, an overall temperature decrease across the unit and pressure drops for gas and liquid in the unit have to be implemented.

The MA synthesis reactor/condenser unit was tested with example calculations. The main parameters in the unit from the point of view of mass balance were seven:

- Alpha values for ASF distribution in products of reactions (3.1) and (3.2);
- Conversion of CO in reactions (3.1), (3.2), (3.3), (3.5) and C_2H_4 conversion in reaction (3.4).

The following quantities were fixed for testing the established model:

- Syngas flow, composition, temperature, pressure;
- MA synthesis liquid product flow, composition, pressure;
- Tailgas concentration of CO_2, C_3H_8, C_2H_6, temperature and pressure.

The model back-calculates the following quantities:

- Both alpha values;
- Conversion of CO in reactions (3.1), (3.2), (3.3), (3.5) and C_2H_4 conversion in reaction (3.4);
- Overall pressure drop in the gas and liquid exit streams;
- Overall temperature decrease.

Table 2 shows the fixed and calculated values of an example calculation with the developed reactor model in $IPSE_{pro}$.

3.2. MA synthesis pilot plant simulation and data validation

The first step in validating the raw experimental data from the Güssing MA synthesis pilot plant is the building up of a reliable process model in $IPSE_{pro}$, by the BG_library upgraded with new objects about MA synthesis. In Fig. 5 the simulation flow chart in $IPSE_{pro}$ PSE of the MA synthesis pilot plant at Güssing is presented.

In the figure the steam reforming simulation part is accentuated with green. The syngas coming from the CHP plant is identified as "raw gas". This gas enters the steam reformer. The measurements of gas composition are on a dry basis, but it is known that it is usually saturated in water at 314 K. In the PSE the water content in raw gas can be calculated by using "gas saturation" units, where the saturation temperature of the humid gas stream can be set, back-calculating the corresponding water fraction. Items about steam injected in the steam reformer can be assumed to be constant in all experiments: 573 K, same pressure of raw gas, and 3.84 Bm^3/h as the operating flow rate. Steam is simulated by a gas connection referring to a gas global where the pure water composition is set. The steam reformer is heated externally over electrical trace heating. In the PSE this is simulated by a modular strategy, being divided into a separate heating operation (simulated by "gas_electrical_heating" unit) and a reaction operation (simulated by "gas_reactor" unit). The reaction temperature is set on the exit stream of the gas reactor (reformed syngas) and heating energy is back-calculated by the "gas_electrical_heating" unit. The conversion of each hydrocarbon is back-calculated by fixing its fraction in the reformed syngas. The pressure before and after the steam reformer is known, so pressure drops can be calculated.

The water scrubbing is marked in blue within the flow chart. The gas scrubbing was simulated with a "gas_water_separation" unit. The exiting "syngas" temperature was set to 275 K (measured value) and this stream is saturated in water, so all water in excess with respect to the thermodynamic limit is separated as "scrubbed water". The temperature of the exiting gas stream is so low that the amount of water remaining in the vapor state can be neglected (usually <0.6%).

The compressor simulation is accentuated in red. The compression is carried out in three stages (simulated by "gas_compressor" units). The inter-cooling stages between the compression steps are simulated by "gas_water_heat_exchanger" units. It is assumed that the compression ratio is equally distributed in the three stages. The syngas temperature after each inter-cooling step is 313 K. The inter-cooling service water is entering at 298 K and exits at 308 K. Each compression stage has the following efficiencies:

- Adiabatic–isentropic: 75%
- Mechanical: 97%
- Electrical: 98%

The syngas inlet and outlet pressure ratio in the first and second compression stages is set. The actual power of compression is calculated as the sum of the actual power requests in each stage.

Table 2
Example calculation of set and calculated values.

Set values			Calculated values		
Syngas H_2	[vol.%dry]	53.0	Alpha alcohols	[–]	0.22
Syngas CO	[vol.%dry]	14.0	Alpha paraffins	[–]	0.00
Syngas CO_2	[vol.%dry]	27.0	CO conversion alcohols	[%]	8.3
Syngas CH_4	[vol.%dry]	6.00	CO conversion paraffins	[%]	4.7
Syngas C_2H_6	[vol.%dry]	0.03	C_2H_4 conversion propanol	[%]	83.2
Syngas C_2H_4	[vol.%dry]	0.02	C_2H_4 hydrogenation	[%]	9.2
Syngas C_3H_8	[vol.%dry]	0.00	Water gas shift	[%]	−1.5
Syngas O_2	[vol.%dry]	0.00	ΔP gas	[MPa]	109
Syngas N_2	[vol.%dry]	1.00	ΔP liquid	[MPa]	0.0
F inlet	[Nm^3/h]	2.1	ΔT	[K]	286
T inlet	[K]	593			
P inlet	[MPa]	11			
F MA liquid	[kg/h]	0.1			
CH_3OH	[mass%]	42.5			
C_2H_5OH	[mass%]	13.4			
H_2O	[mass%]	37.3			
P product	[MPa]	11			
Tailgas CO_2	[vol.%dry]	28.3			
Tailgas C_3H_8	[vol.%dry]	0.00			
Tailgas C_2H_6	[vol.%dry]	0.03			
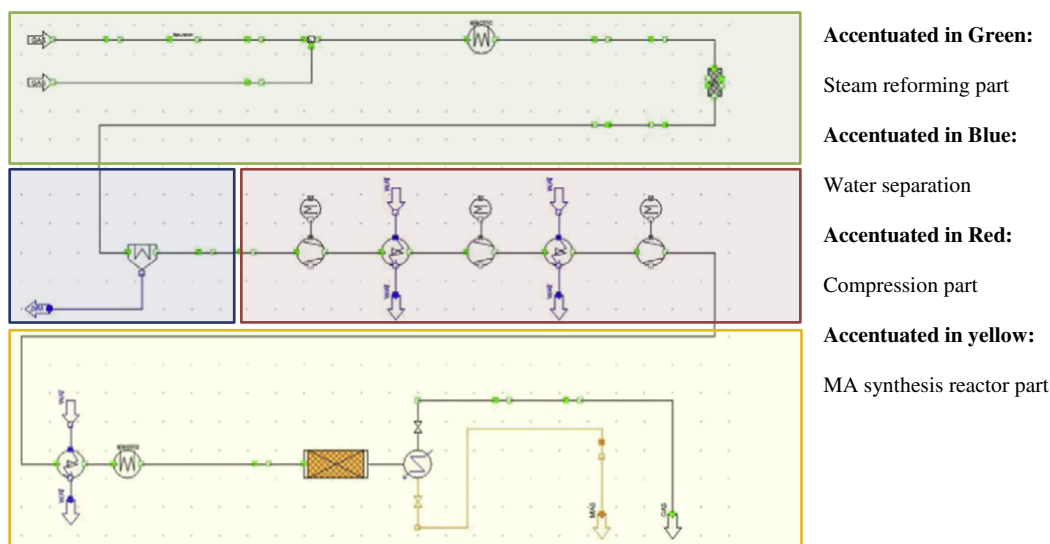
Fig. 5. Simulation of whole Güssing MA synthesis pilot plant in IPSE$_{pro}$ PSE.

Accentuated in Green:

Steam reforming part

Accentuated in Blue:

Water separation

Accentuated in Red:

Compression part

Accentuated in yellow:

MA synthesis reactor part

The simulation of the MA synthesis reactor and condenser is marked in yellow. A "gas_electrical_heater" is used before the MA synthesis unit in order to reach the reaction temperature, the temperature is set for the "syngas" stream.

Analysis of the MA synthesis liquid product showed the presence of other compounds beside alcohols and water (benzene, toluene and unidentified compounds). They are not accounted for in the model because they aren't important for the purpose of closing the mass balance. Benzene and toluene are only a dilution. The respective mass flow of unidentified compounds was subtracted from the total mass flow to correct the simulation results. The accounted for components and flows consider only water and alcohols, without the contributions of all other components.

3.3. Validation results

The PSE model for the MA synthesis pilot plant was used for validation of experimental data to obtain a perfectly closed mass and energy balance by IPSE$_{pro}$ simulation. The validation data is given to the PSE process model as "measurement" inputs, creating a data redundancy. PS Validate varies all "measurements" in such a way that PSE model equations are respected, but the validated values are as close as possible to the raw experimental data. A "measurement" setting must be declared with its absolute tolerance range within which PS Validate tries to make its adjustment.

Table 3 shows the relative tolerance for each kind of experimental data, based on the reliability of the corresponding measurement instrument.

Table 4 is showing the validation of experimental data yielded on 21/06/2012. The used experimental conditions were a pressure of 11 MPa and reaction temperature of 593 K. In the column "Measure" the measured quantities can be seen. The measured quantities are also in correlation to presented sampling points in Fig. 2. The measured components are visible in the column "Component". The given tolerances are corresponding to Table 3. The experimental values, the validated values by IPSE$_{pro}$ and the calculated relative error between measured and validated values are shown in the last three columns of the table.

The corrections to measured values of inlet gas flow, outlet gas flow and product mass flow are marginal and within given tolerance of 15%. IPSE$_{pro}$ calculated a noticeable correction for the C_2H_6 amount at the outlet of the MA synthesis reactor. The measured value of C_2H_6 was corrected by 110%. Also the amount of N_2 was corrected at the inlet and outlet of the reactor. The corrections to the other gas components

were within the given tolerance of 5%. The corrections to MA product composition are marginal.

Table 5 shows an overview about obtained relative errors between experimental and validated values for the experiments carried out in the year 2012. The table gives a good overview about the corrections which were carried out by IPSE$_{pro}$ to obtain a closed mass balance for the corresponding experiments. The given tolerance for each measurement in percent can be seen in the column "Tolerance".

During the process of validation all process hypotheses developed for the PSE MA synthesis Güssing pilot plant simulation remained valid. An evaluation of presented data in Table 5 shows that the corrections between measured and validated values are normally within the given tolerance range. The simulation model is very accurate about MA synthesis liquid product composition. The corrections are, in the worst case, very close to the given measurement tolerance of 10% and usually minor, at about 1% or less. The corrections on gas and liquid flow rates are always less than 15% of the original value, so they're very much inside the tolerance given for gas flow meters and indirect MA liquid flow calculation.

The validations of gas composition are overall satisfactory, but the relatively low values for hydrocarbon concentrations of C_2H_6 and C_2H_4 are often far from the original values on a relative scale. Significant corrections had to be carried out for the amount of C_2H_6 after MA synthesis reactor by IPSE$_{pro}$ to close the mass balance. The corrections are between 2 and 4400%. Nevertheless, the absolute magnitude of the original values and their corrected versions is very small and always below 0.3 vol.%dry, the validation is not altogether influenced. Measurement inaccuracies are more likely than some unaccounted for chemical reaction in IPSE$_{pro}$. The corrections for the N_2 amount before and after MA synthesis reactor are also exceeding the given tolerance of 5%. The corrections are between 0 and maximum of 55%. The influence of N_2 corrections on the overall validation result is negligible.

Table 3
Relative tolerances for validation measurement inputs.

Measurement	Relative tolerance [% of measurement]
Temperature	2.5
Pressure	2.5
Flow	15
Gas composition	5
Liquid composition	10

Table 4
Validation of experimental data yielded on 21/06/2012.

Measure	Component	Tolerance [%]	21/06/12		
			Experimental	Validation	Rel. Error [%]
Normal flow synthesis gas before MAS reactor					
F1		[Nm^3/h]	1.44	1.39	−3
Gas dry composition before MAS reactor					
GC2	H$_2$	[vol.%dry]	48.8	49.6	2
GC2	CO	[vol.%dry]	14.2	13.6	−4
GC2	CO$_2$	[vol.%dry]	27.5	27.4	0
GC2	CH$_4$	[vol.%dry]	7.64	7.25	−5
GC2	C$_2$H$_6$	[vol.%dry]	0.00	0.00	0
GC2	C$_2$H$_4$	[vol.%dry]	0.35	0.35	0
GC2	C$_3$H$_8$	[vol.%dry]	0.00	0.00	0
GC2	N$_2$	[vol.%dry]	1.51	1.74	16
Normal flow synthesis gas after MAS reactor					
F2		[Nm^3/h]	1.34	1.29	−4
Gas dry composition after MAS reactor					
GC3	H$_2$	[vol.%dry]	47.9	47.4	−1
GC3	CO	[vol.%dry]	11.7	12.1	3
GC3	CO$_2$	[vol.%dry]	29.5	29.7	1
GC3	CH$_4$	[vol.%dry]	8.23	8.65	5
GC3	C$_2$H$_6$	[vol.%dry]	0.13	0.26	110
GC3	C$_2$H$_4$	[vol.%dry]	0.00	0.00	0
GC3	C$_3$H$_8$	[vol.%dry]	0.00	0.00	0
GC3	N$_2$	[vol.%dry]	2.46	1.88	−24
Liquid mass flow					
F MA liquid		[kg/h]	0.04	0.04	7
Liquid composition					
MA composition	CH$_3$OH	[mass%]	44.7	44.8	0
MA composition	C$_2$H$_5$OH	[mass%]	14.0	14.2	1
MA composition	C$_3$H$_7$OH	[mass%]	14.2	14.2	0
MA composition	H$_2$O	[mass%]	27.1	26.7	−1

In Table 6 the validated mass balance for the considered example experiment on 21/06/2012 is visible. The mass balance was calculated over the MA synthesis reactor and condenser.

Table 7 gives an overview about the validated MA synthesis reactor performance of several experiments from 2012. A validated experiment from 2014 with a second batch of MoS$_2$ based catalyst is also displayed for the reason of comparability. In accordance with the literature [16], WGS free based items were used to evaluate the performance of the MA synthesis reactor. The CO conversion reached on a WGS free base with the first batch of catalyst was around 18% at 593 K. Around 28% CO conversion at WGS free based could be achieved with the new batch of catalyst at a reaction temperature of 583 K.

Table 5
Overview about obtained relative error validation.

Measure	Component	Tolerance [%]	Relative error [%]					
			19/01/12	14/02/12	20/06/12	21/06/12	06/09/12	20/09/12
F1		15	−1	−11	1	−3	−1	2
GC2	H$_2$	5	3	0	0	2	−6	8
GC2	CO	5	−9	2	1	−4	3	−8
GC2	CO$_2$	5	5	0	0	0	9	1
GC2	CH$_4$	5	−7	−3	−2	−5	−2	−5
GC2	C$_2$H$_6$	5	0	0	0	0	−100	0
GC2	C$_2$H$_4$	5	475	−15	0	0	0	400
GC2	C$_3$H$_8$	5	0	0	0	0	0	0
GC2	N$_2$	5	−29	26	0	16	23	−47
F2		15	2	−10	0	−4	0	3
GC3	H$_2$	5	−1	−3	0	−1	3	−4
GC3	CO	5	11	4	−1	3	0	8
GC3	CO$_2$	5	5	9	0	1	−1	0
GC3	CH$_4$	5	5	2	2	5	1	6
GC3	C$_2$H$_6$	5	58	2	3400	110	1520	4400
GC3	C$_2$H$_4$	5	0	9	0	0	0	0
GC3	C$_3$H$_8$	5	0	0	0	0	0	0
GC3	N$_2$	5	−55	−29	−12	−24	−33	1
F MA liquid		15	0	15	0	7	0	−6
MA composition	CH$_3$OH	10	0	−3	0	0	0	1
MA composition	C$_2$H$_5$OH	10	0	−3	0	1	0	1
MA composition	C$_3$H$_7$OH	10	0	12	0	0	0	0
MA composition	H$_2$O	10	0	0	0	−1	0	−2

Table 6
Validated mass balance for experiment on 21/06/2012.

Stream		Before compression	Before MAS reactor/condenser	After MAS reactor/condenser	MAS product
General properties					
State		Gas	Gas	Gas	Liquid
T	[K]	275	593	307	307
p	[MPa$_a$]	0.11	11.00	0.11	11.0
v	[m^3/kg]	1.17	0.02	1.22	1E−03
F	[kg/h]	1.16	1.16	1.15	0.04
	[Nm^3/h]	1.39	1.39	0.13	/
Q	[m^3/h]	1.35	0.03	1.36	5E−05
Gas dry composition					
H$_2$	[vol.%dry]	49.6	49.6	47.6	/
CO	[vol.%dry]	13.6	13.6	12.0	/
CO$_2$	[vol.%dry]	27.4	27.4	29.7	/
CH$_4$	[vol.%dry]	7.30	7.30	8.60	/
C$_2$H$_6$	[vol.%dry]	0.00	0.00	0.26	/
C$_2$H$_4$	[vol.%dry]	0.35	0.35	0.00	/
C$_3$H$_8$	[vol.%dry]	0.00	0.00	0.00	/
O$_2$	[vol.%dry]	0.00	0.00	0.00	/
N$_2$	[vol.%dry]	1.70	1.70	1.90	/
H$_2$/CO ratio	[#]	3.60	3.60	3.90	/
Liquid composition					
CH$_3$OH	[mass%]	/	/	/	44.9
C$_2$H$_5$OH	[mass%]	/	/	/	14.2
C$_3$H$_7$OH	[mass%]	/	/	/	14.2
C$_4$H$_9$OH	[mass%]	/	/	/	0
C$_5$H$_{11}$OH	[mass%]	/	/	/	0
H$_2$O	[mass%]	/	/	/	26.7

The considered parameters in the table are:

- Conversions in all modeled reactions ($X_{CO}^{\text{side propanol}}$, X_{CO}^{WGS}, $X_{C_2H_4}^{\text{side propanol}}$, $X_{C_2H_4}^{\text{hydrogenation}}$, $X_{C_2H_4}$)

Table 7
Validated MA synthesis reactor performances of several experiments.

Day of experiment		19/01/12	14/02/12	20/06/12	21/06/12	16/09/14
Catalyst		MoS$_2$ (A)	MoS$_2$ (A)	MoS$_2$ (A)	MoS$_2$ (A)	MoS$_2$ (B)
Conditions						
T	[K]	558	583	593	593	583
P	[MPa$_a$]	10	10	11	11	11
SV	[Nl/l h]	1364	1849	1024	928	1067
(H$_2$/CO)$_{\text{syngas}}$	[#]	3.6	3.8	3.6	3.6	3.4
Conversions						
$X_{CO}^{a,1}$	[%]	2.3	2.4	5.7	7.0	10.0
$X_{CO}^{a,2}$	[%]	0.7	0.9	2.4	3.1	7.3
$X_{CO}^{a,3}$	[%]	0.2	0.3	1.0	1.3	6.4
X_{CO}^{a}	[%]	3.1	3.7	9.1	11.5	23.7
$X_{CO}^{p,1}$	[%]	0.0	0.5	4.9	5.5	2.7
$X_{CO}^{p,2}$	[%]	0.0	0.2	0.0	0.0	0.9
$X_{CO}^{p,3}$	[%]	0.0	0.0	0.0	0.0	0.3
X_{CO}^{p}	[%]	0.0	0.7	4.9	5.5	3.9
$X_{CO}^{\text{side propanol}}$	[%]	0.1	0.3	0.7	0.8	0.0
$X_{CO, \text{WGS free}}$	[%]	3.2	4.6	14.7	17.7	27.7
X_{CO}^{WGS}	[%]	−1.0	−1.1	0.9	0.5	3.7
X_{CO}	[%]	2.2	3.5	15.6	18.1	31.3
$X_{C_2H_4}^{\text{side propanol}}$	[%]	79.3	18.8	28.3	29.6	1.2
$X_{C_2H_4}^{\text{hydrogenation}}$	[%]	0.0	3.9	70.0	69.6	97.0
$X_{C_2H_4}$	[%]	79.3	22.7	98.2	99.2	98.3
Selectivities WGS free based						
$S_{CO}^{a,1}$	[%]	70.2	51.6	38.8	39.8	36.2
$S_{CO}^{a,2}$	[%]	20.2	20.1	16.3	17.5	26.5
$S_{CO}^{a,3}$	[%]	5.0	7.3	6.5	7.4	23.0
S_{CO}^{a}	[%]	95.3	79.0	61.7	64.8	85.7
$S_{CO}^{p,1}$	[%]	0.3	11.0	33.6	31.0	9.9
$S_{CO}^{p,2}$	[%]	0.3	3.2	0.1	0.0	3.3
$S_{CO}^{p,3}$	[%]	0.3	0.9	0.0	0.0	1.0
S_{CO}^{p}	[%]	0.9	15.1	33.7	31.0	14.2
$S_{CO}^{\text{side propanol}}$	[%]	3.7	5.8	4.6	4.2	0.0

- CO conversion to Cj alcohol within primary alcohol formation (X_{CO}^a, $X_{CO}^{a,1}$, $X_{CO}^{a,2}$, $X_{CO}^{a,3}$)
- CO conversion to Cj paraffin within FT paraffin formation (X_{CO}^p, $X_{CO}^{p,1}$, $X_{CO}^{p,2}$, $X_{CO}^{p,3}$)
- CO conversion, WGS free ($X_{CO, \text{WGS free}}$)
- Total CO conversion (X_{CO})
- CO selectivity, side propanol ($S_{CO}^{\text{side propanol}}$)
- CO selectivity, WGS free based to Cj alcohol within linear primary alcohol formation (S_{CO}^a, $S_{CO}^{a,1}$, $S_{CO}^{a,2}$, $S_{CO}^{a,3}$)
- CO selectivity, WGS free based to Cj paraffin FT paraffin formation (S_{CO}^p, $S_{CO}^{p,1}$, $S_{CO}^{p,2}$, $S_{CO}^{p,3}$).

The influence of reaction temperature on CO conversion is visible, but there are not enough experimental data points to infer a quantitative dependence. The tendencies are similar to data in the literature [8] over the examined temperature range:

- The CO conversion in linear primary alcohols, FT paraffins, and side 1-propanol from C$_2$H$_4$ formation increases with rising reaction temperature.
- The CO selectivity, WGS free based, towards FT paraffin formation increases at the expense of linear alcohol formation, while, for 1-propanol from C$_2$H$_4$, it remains nearly constant.
- Within linear primary alcohol formation products, the total CO selectivity WGS free based decrease is mainly related to methanol reduction, while ethanol selectivity remains constant and 1-propanol has a small increase. The increase in reaction temperature pushes the production of higher alcohols.
- Within FT paraffin formation products, the CO conversion WGS free based is directed nearly entirely to the production of CH$_4$.

4. Conclusion

At the Güssing CHP plant location the company Bioenergy2020+ GmbH is operating a MA synthesis pilot plant for experiments with real synthesis gas from wood chip steam gasification. Experiments

have been performed at this pilot plant since 2011. Unfortunately, because of low conversion rates, unstable operating conditions and measurement inaccuracies, closing of the mass and energy balance was not possible by using raw experimental data. Validation by a software simulation approach was chosen as a solution for this problem. Validation is the reconciliation by the least squares method of raw experimental measurements of a phenomenon with its mathematical model, based on mass and energy conversion principles.

The stationary process simulation software $IPSE_{pro}$ was used as a tool for this purpose. With the software package tool MDK a "black-box" model of the reactor and condenser was established. Several simplifications and hypotheses have been made. Only quantitatively relevant reactions are considered in the model: MA formation, FT paraffin formation, WGS, the C_2H_4 to 1-propanol side reaction and C_2H_4 hydrogenation. ASF distribution is assumed for alcohols and paraffins. The reactor and condenser were modeled in one unit, in such a way as to consider alcohols only in the liquid state. Water and alcohols are completely condensed, constituting the liquid product. The other components are permanent gases constituting the tailgas.

The PSE model is very close to the actual MA synthesis pilot plant and all assumptions are taken from the experimental knowledge. Validation was carried out successfully within the software module PS Validate. All experiments were validated successfully. The model is very accurate about MA synthesis liquid product compositions and all measured flows. Regarding gas composition, there are some difficulties in reconciling the measured low hydrocarbon concentrations. There are not enough experimental points to find quantitatively reliable laws for the influence of the operative parameters, but anyway the tendencies shown by the validated data about alcohol and paraffin production are compatible with literature information. ASF distribution and the side reaction of C_2H_4 to 1-propanol fit very well the final MA product composition. The constancy of CO conversion in this side reaction suggests that the hypothesis about this side reaction is true. WGS and C_2H_4 hydrogenations have no clear tendencies.

The modeling and validation of MA synthesis in $IPSE_{pro}$ did provide satisfactory results. A deeper knowledge about the reliability of experimental measurements in the Güssing MA synthesis pilot plant has been achieved. The model and data validation presented in this publication will be a good starting point for further studies of MA synthesis scale-up and economic feasibility.

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