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ORIGINAL ARTICLE

Waste biomass to methanol optimisation of gasification agent to feed ratio

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Abstract

Residues from agriculture and forest maintenance (lignocellulosic waste biomass) create a huge source of renewable energy and valuable materials. Gasification of this waste provides combustible gases consisting mainly of H_2, CO and CO_2, which can be used as syngas feed for methanol synthesis after treatment. Oxygen, steam or their mixtures can be used as gasifying agents in the biomass to methanol process. One of the most important parameters with crucial effect on gas composition and reactor temperature is the gasifying agent to feed mass flow ratio. In this work, gasification process of two samples of mixed agricultural waste, gas treatment and synthesis of methanol from the syngas produced was designed and simulated in the Aspen Plus environment. Three different cases were investigated: (1) only oxygen as gasifying agent, (2) oxygen and steam as gasifying agents without steam recycling and (3) oxygen and steam as gasifying agents with steam recycling. Samples of mixed agricultural waste consisted of corn leaves and stalks, wheat straw, barley straw, sunflowers and wood chips were characterised by proximate, ultimate and calorimetric analysis. Oxygen and steam flows were optimised to achieve maximum theoretical yield of methanol while maintaining the gasifier temperature, equal to, at least 900 °C. The best methanol to biomass ratio (MBR) of 0.43 was reached for a sample with lower moisture and ash content when both oxygen and steam were used as gasifying agents. The optimal oxygen to biomass ratio (OBR) was 0.57, and the steam to biomass ratio (SBR) was 0.89.

Keywords Waste biomass · Gasification · Methanol

1 Introduction

Waste biomass comes in form of forest maintenance materials, residues from agriculture, dedicated crops and many other sources [1]. Biomass represents up to 14% of the world's annual energy consumption, and it is the third largest primary energy resource after coal and oil [2]. The heat of combustion of biomass ranges from 8 MJ/kg to 20 MJ/kg [3] depending on its composition and moisture content. Although the major attention has been paid to energy recovery from biomass, conversion to more valuable chemicals is more attractive but also a more challenging biomass use.

Methanol is one of the basic chemicals used in many applications. Recently, more than 100 million metric tons of methanol have been produced worldwide [4]. Around 90% of this amount comes from natural gas [5]. Although steam reforming of natural gas represents the basic and cheapest technology for methanol production, increased attention has been paid to the search for alternative renewable sources for methanol syntheses. The efforts for industrial methanol production from alternative raw materials date back from the early 1990s by projects such as the Hynol project [6] in the USA, Bio-Meet and Bio-Fuels projects in Sweden [7] and Enerkem company project in Canada [8] which currently plan, in cooperation with other partners, to build a relatively large waste to methanol plant near Rotterdam.

By biomass gasification, a combustible gas consisting mainly of H_2, CO and CO_2 can be produced. Product gas can be combusted to produce heat and electricity, or it can be used as a synthesis gas for the production of chemicals such as methanol. Generally, air, oxygen, steam or their mixtures can be used as gasifying agents in biomass gasification. However, if the goal is methanol synthesis, oxygen in combination with steam is used

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as the gasifying agent to prevent N_2 content in the syngas. Gaseous products also contain fine particles, small amounts of light hydrocarbons, tar and traces of H_2S, NH_3 and HCl. Before using the gas in methanol synthesis, the contaminants have to be removed. Fine particles have to be removed because they cause fouling and erosion of piping and production units. Fly ash is normally separated in cyclones, barriers or electrostatic filters. Gas tar content should be reduced below the limits acceptable for appropriate technology (from 1 to 500 mg/Nm^3) [9]. Secondary physical or chemical tar removal means have to be applied to prevent combustion engines and turbines fouling or catalyst poisoning in downstream production units [10]. Although the concentration of H_2S, NH_3 and HCl in product gas is low, it can still cause significant device corrosion and catalyst poisoning. Concentration of these gases has to be lowered below a certain level which is specified by the unit's construction material and the catalyst used. When synthesis gas is used for methanol production, concentration of H_2S has to be below 100 ppb, concentration of HCl below 1 ppb and concentration of NH_3 below 10 ppb [11].

For the synthesis of each mole of methanol (CH_3OH), 1 mol of CO and 2 mol of H_2 are required. Of course, hydrogenation of CO_2 also takes place. Several researches report that in a traditional methanol production process with the Cu/ZnO/Al2O3 catalyst, maximum methanol production is reached at CO_2 concentration of 2–5 mol% of total carbon [12]. However, Grabow and Mavrikakis [13] studied the mechanism of methanol synthesis on Cu from a CO_2 rich $CO/CO_2/H_2$ mixture and concluded that under typical industrial methanol synthesis conditions, CO_2 hydrogenation is responsible for approximately 70% of the methanol amount produced.

The required H_2/CO ratio can be obtained by the control of the process conditions in the gasifier or by secondary operations. The presence of steam in the gasifier and primary or secondary catalysis can increase the H_2/CO ratio [14]. Water-gas shift reaction at temperatures around 300 °C can be used as additional operation for H_2/CO increase [15].

The use of appropriate gasification technology and control of optimal process conditions in the gasifier have a crucial effect on syngas composition and contaminant content. Process mathematical modeling and computer simulation can be used to look for optimal process conditions and decrease the total number of experiments required for the gasification process design. Aspen Plus® has been used by different authors to model biomass gasification and methanol synthesis in recent years. Trop et al. [16] provided an Aspen simulation and economic evaluation of methanol production from a mixture of torrefied biomass and coal. They concluded that reduction in carbon taxes can be the main motivation of coal replacement by torrefied biomass. A relatively complete Aspen simulation of biomass to methanol was published by Yang et.al. [15]. The authors used a simple equilibrium model for a dual-stage entrained-flow gasifier and achieved a methanol yield of 18.5 mol/kg of dry biomass. The equilibrium model of gasification is based on Gibbs free energy minimisation and takes into account only thermodynamic limitations. This model disregards any reaction or transport rate mechanisms [17]. However, equilibrium model is reliable and provides an acceptable agreement with the experimental data at gasifier temperatures above 800 °C [18, 19]. Dual-stage entrained-flow gasifiers work at higher temperatures than 800 °C, and fine particle size is used on the gasification stage. Therefore, conditions in such a reactor are not very far from the equilibrium conditions. The equilibrium model was used also by Pala et.al. [20] using Aspen Plus and an equilibrium model; the authors simulated syngas production from different types of biomass and observed the impact of the steam to biomass ratio on the amount of produced hydrogen. The authors concluded that CO conversion decreases with the increasing water-gas shift temperature between 250 °C and 400 °C, and the CO_2 conversion increases with the increasing reverse water-gas shift temperature between 450 °C and 900 °C.

If gasification conditions do not meet the equilibrium ones, a more complex model considering also process kinetics and heat and mass transfer is used. Feng et al. [21] proposed a one dimensional kinetic model for both gasification and methanol synthesis processes and found that 35.4% of carbon atoms of the biomass are delivered into methanol. Pauls et al. [22] made a kinetic model in Aspen Plus which included gasification kinetics, tar formation kinetics and hydrodynamic model of the gasifier. The authors concluded that a kinetic model is better for the estimation of CO and H_2 content in product gases than the previously used empirical one.

Other literature sources deal with modeling of methanol production via gasification of different feeds such as biomass [23–25], municipal solid waste [26], poplar wood [27], and black liquor [28]. A detailed Aspen Plus simulation of all processes from waste gasification to methanol synthesis including gas treatment processes and gas compression is provided in a previous work [29]. Refused-derived fuel (RDF) was used as the raw material. An equilibrium model modified by an experimentally based empirical correlation for gas tar content, and recalculation of product yields based on atom balance was applied. Arteaga-Pérez et al. [30] used a quasi-equilibrium model in a techno-economic analysis of biomass gasification integrated in methanol and CNG (compressed natural gas) production. The authors used temperature correction to calculate equilibrium composition and validated the model against experimental data showing a good coherence of the quasi-equilibrium model with experimental data from different sources.

Despite of recent attentions to research in methanol production from biomass, a number of challenges still remain. Heterogeneous and scattered raw material, requirement for gas cleaning and specific value of H_2/CO ratio in the syngas, as well as factors affecting process efficiency in reaching better process economy, need more theoretical and experimental research.

Table 1 Biomass samples composition

Weight fraction (wt%)	Wheat straw	Barley straw	Corn leaves and stalks	Sunflowers	Wood chips
Sample 1	9.238	13.840	15.350	39.092	22.480
Sample 2	14.497	14.499	53.410	12.160	5.430

In this work, gasification process of two samples of mixed agricultural waste for methanol production was designed and simulated in the Aspen Plus environment. Oxygen and steam were used as gasifying agents. Samples of mixed agricultural waste consisted of corn leaves and stalks, wheat straw, barley straw, sunflowers and wood chips. Oxygen to biomass ratio (OBR) and steam to biomass ratio (SBR) were optimized to achieve maximum theoretical yield of methanol (methanol to biomass ratio – MBR) while maintaining the temperature in the gasifier equal to at least 900 °C. In a variant of solutions, unreacted steam and produced tar were fed back to the gasifier to achieve better steam and tar conversion. The effect of recycling all steam leaving the gasifier on reactor temperature, OBR and MBR was observed.

2 Raw material characterization

Two mixtures of agricultural waste biomass composed of wheat straw, barley straw, corn leaves, corn stalks, sunflowers and wood chips were considered as raw material for methanol synthesis in this study. Composition of each sample is given in Table 1. Each component of waste biomass mixtures was the subjected to proximate, elemental and calorimetric analyses. For mixed samples (Samples 1 and 2 in Table 2), these parameters were calculated based on the values for individual components and component fractions in the sample. Information on proximate and elemental composition and heating value was used as input data in the Aspen simulation.

Table 2 shows the moisture and ash content, ultimate analysis and higher heating value (HHV) of both mixed samples. Moisture content of the samples was measured using a standard procedure based on EN ISO 18134-3: 2015. Elemental composition was estimated by a Vario Macro Cube ELEMENTAR elemental analyzer. Ash content was estimated using thermogavimetric data obtained by a simultaneous TG/DSC analyzer (Netzsch STA 409 PC Luxx. Germany). Higher heating value (HHV) was measured using an FTT isoperibolic calorimetric bomb (Fire Testing Technology Limited).

Composition of the samples was selected based on their availability in two specific regions in Slovakia. Despite significant differences in the sample composition, differences in the parameters of final mixtures are not significant because of mutual compensation between the components. For example, high calorific value of wood chips in Sample 1 is compensated by lower calorific value of sunflower. The most visible differences were observed in the moisture and ash content of the samples. Sample 1 had higher ash and moisture content than Sample 2.

3 Waste to methanol Aspen Plus simulation model

As shown in Fig. 1, a waste to methanol plant can be divided into four subsections. In the first step, biomass is gasified in a gasification plant. Then, the produce syngas is treated in a gas treatment plant where syngas suitable for methanol production is produced. Syngas with the required composition is compressed in a gas compression plant and then introduced to a methanol plant where methanol is produced.

Detailed Aspen simulation of all steps including material and energy balances, phase equilibrium calculations, chemical reaction equilibrium, material and energy integration and process economic evaluation is given in a previous work [23]. The present paper is focused on the effect of gasifying agent (oxygen and/or steam) to biomass ratio as well as of feed composition on process efficiency given by the methanol to biomass ratio. For this reason, we focus only on the model of the gasification section.

An equilibrium model based on minimisation of Gibbs free energy for the gasifier was considered. The model basic equations are presented below [23]:

The Gibbs free energy change of a reaction system is given as

$$\Delta_r G = \Delta_r G^\circ + \mathrm{R}T \ln \prod_i a_i^{\nu_i} \tag{1}$$

where, $\Delta_r G^\circ$ is the standard (reference) Gibbs free energy, a_i is the activity of component i, ν_i is the stoichiometric coefficient of component i, R is the gas constant and T the temperature (K). In equilibrium state, $\Delta_r G = 0$, and from Eq. 1 follows:

$$\Delta_r G^\circ = -\mathrm{R}T \ln K_e \tag{2}$$

where K_e is the equilibrium constant of the chemical reaction.

$$K_e = \prod_i a_i^{\nu_i} \tag{3}$$

Standard Gibbs free energy can be calculated from the standard Gibbs free energies of formation, $\Delta_f G_i^\circ$, of individual components as:

Table 2 Biomass property summary

Biomass	Moisture (wt%)	Ash (dry basis wt%)	Ultimate analysis (wt% dry basis)					HHV (MJ/kg dry basis)
			C	H	N	S	O	
Wheat straw	1.91	4.90	42.80	5.44	0.60	0.00	46.26	16.80
Barley straw	1.94	6.90	49.70	6.90	1.00	0.70	34.80	16.96
Corn leaves and stalks	6.05	2.08	50.88	5.26	0.74	0.19	40.85	16.97
Sunflowers	14.60	7.31	45.38	5.66	0.26	2.22	39.16	14.68
Wood chips	7.04	0.96	52.70	5.34	0.50	0.00	40.50	18.84
Sample 1	8.66	4.80	48.23	5.68	0.52	0.99	39.77	16.48
Sample 2	5.95	3.76	48.97	5.58	0.69	0.47	40.53	16.77

$$\Delta_r G^\circ = \sum_i \nu_i \Delta_f G_i^\circ \tag{4}$$

If the standard heat of formation, $\Delta_f H_i^\circ$, and the standard absolute entropy, S_i°, of components are available, $\Delta_r G^\circ$ can be calculated as

$$\Delta_r G^\circ = \sum_i \nu_i \Delta_f H_i^\circ - T \sum_i \nu_i S_i^\circ \tag{5}$$

In this work, a dual pyrolysis/gasification system with secondary catalytic decomposition of tars was considered. In the first step, biomass is decomposed to char, tar and gas, and in the second step, the producer gas main components are produced via a number of reactions. The main reactions of the gasification steps can be concluded as:

Combustion reactions

$$C + 0,5O_2 \rightarrow CO \left(\Delta H^\circ_{298} = -111\ \text{kJ.mol}^{-1}\right) \tag{R1}$$

$$CO + 0,5O_2 \rightarrow CO_2 \left(\Delta H^\circ_{298} = -283\ \text{kJ.mol}^{-1}\right) \tag{R2}$$

$$H_2 + 0,5O \rightarrow H_2O \left(\Delta H^\circ_{298} = -242\ \text{kJ.mol}^{-1}\right) \tag{R3}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \left(\Delta H^\circ_{298} = -394\ \text{kJ.mol}^{-1}\right) \tag{R4}$$

$$C_nH_m + (n + m/4)O_2 \rightarrow nCO_2 + m/2H_2O \left(\Delta H^\circ_{298} < 0\ \text{kJ.kmol}^{-1}\right) \tag{R5}$$

Gasification reactions

$$C + CO_2 \leftrightarrow 2CO \left(\Delta H^\circ_{298} = 131\ \text{kJ.mol}^{-1}\right) \tag{R6}$$

$$C + H_2O \leftrightarrow CO + H_2 \left(\Delta H^\circ_{298} = 172\ \text{kJ.mol}^{-1}\right) \tag{R7}$$

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \left(\Delta H^\circ_{298} = 206\ \text{kJ.mol}^{-1}\right) \tag{R8}$$

$$C_nH_m + nH_2O \rightarrow nCO + (n + m/2)\ H_2 \left(\Delta H^\circ_{298} > 0\ \text{kJ.kmol}^{-1}\right) \tag{R9}$$

$$C_nH_m + nCO_2 \rightarrow 2nCO + m/2H_2 \left(\Delta H^\circ_{298} > 0\ \text{kJ.kmol}^{-1}\right) \tag{R10}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \left(\Delta H^\circ_{298} = -75\ \text{kJ.kmol}^{-1}\right) \tag{R11}$$

$$C + 2H_2 \leftrightarrow CH_4 \left(\Delta H^\circ_{298} = -41\ \text{kJ.kmol}^{-1}\right) \tag{R12}$$

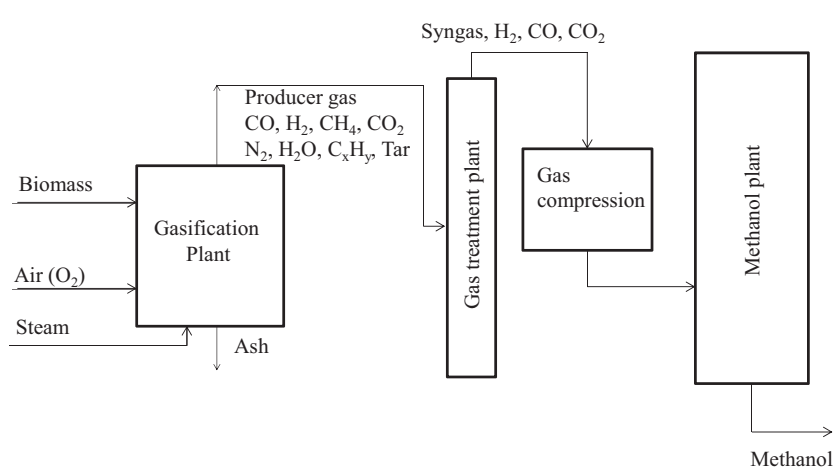

Fig. 1 Biomass to methanol production steps

The equilibrium model provides good results at temperatures above 1000 °C but it fails at reactor temperatures below 800 °C [19]. At lower temperatures, the real gas composition can be significantly different from the equilibrium composition. Therefore, the equilibrium model was modified by an experimentally based empirical correlation for tar formation and recalculation of the product yields to meet the balance of atoms based on Eq. R13.

$$\mathrm{CHxOyNz\,Sr} + \mathrm{s(O2)} \rightarrow \mathrm{x_1H_2} + \mathrm{x_2CO} + \mathrm{x_3CO_2} + \mathrm{x_4H_2O} + \mathrm{x_5CH_4} + \mathrm{x_6CHx'Oy'Nz'Sr'} + \mathrm{x_7H_2S} + \mathrm{x_8NH_3} \quad \text{(R13)}$$

Here, *x, y, z* and *r* represent the number of atoms of hydrogen, oxygen, nitrogen and sulphur, respectively, based on a single atom of carbon in the solid fuel, *s* represents moles of oxygen used per moles of solid fuel and x_1, x_2, x_3, x_4, x_5, x_6, x_7 and x_8 are the stoichiometric coefficients of each corresponding product. While *x', y', z'* and *r'* show the number of atoms of hydrogen, oxygen, nitrogen and sulphur, respectively, based on a single atom of carbon in tar. A system of algebraic equations consist of balance equations of each atom type, global balance given by Eq. R13 and equilibrium constant equations of at least four reactions from R6-R12, enabling the estimation of the stoichiometric coefficients x_1-x_8. Two RYield reactor models (PYRO1 and PYRO2 in Fig. 2) in combination with an RGibss (R-GASIFI in Fig. 2) reactor model and a calculator tool were used to describe the gasifier model in Aspen Plus. For all other unit operations, standard Aspen Plus models were applied. In the PYRO1 reactor model, biomass was decomposed into elements, water and ash according to composition given in Table 2. In the second RYield reactor model (PYRO2), recycled tar was decomposed. An Aspen calculator block was used to calculate the amount of tar formed at the conditions in the gasifier and to control the atoms' balance in the gasifier. RGibbs reactor model (R-GASIFI) was applied to calculate the equilibrium composition of syngas. The tars represented by naphthalene had to be inert in the RGibbs reactor model because at equilibrium conditions, only traces of naphthalene are present in syngas at high temperatures.

Other assumptions include 100% conversion of biomass to gases and ash, only CO, H_2, CO_2, H_2O, CH_4, NH_3, HCl, H_2S and N_2 are considered as gas components, no heat loss from the gasifier and heat exchangers was considered, and gasifier worked at atmospheric pressure.

A flow diagram of gasification, which represents the first step of biomass to methanol process, is shown in Fig. 2.

Pure oxygen and steam were used as gasifying agents. Steam presence ensures increased H_2 yield, and the use of pure oxygen led to low concentrations of N_2, CH_4 and tars in the product gas. Low pressure preheated steam of 300 °C was used in the gasifier. Temperature of the biomass stream (BIOMASS in Fig. 2), supply water for steam generation (S-WATER1) and oxygen stream (OXYGEN) was set to 20 °C. Gas leaving the gasifier was led to a cyclone (ASHSPLIT) where ash was separated; it was cooled in a heat exchanger network (HE1-HE4) where steam used in the gasifier was produced. In one of the studied operation regimes, condensed tars and water were recycled back to the gasifier.

In this work, auto-thermal gasification of biomass was considered. The heat required for biomass decomposition was obtained by partial combustion of biomass (energy streams R-HEAT1 and R-HEAT2). The gasifier temperature depends on the oxygen to biomass ratio. Also, the steam to biomass ratio, biomass heating value and biomass moisture content can significantly influence the reactor temperature. In all cases studied in this work, the cold gas efficiency (CGE), defined as the heating value of produced gas divided by the heating value of biomass, was between 68 and 75%. The heat required for steam generation used in the gasifier was obtained by process heat integration (HE1 and HE2).

4 Results and discussion

Three different operating regimes were simulated and compared to evaluate influence of the gasifying agent to biomass ratio (OBR and SBR) on the methanol to biomass ratio (MBR): in the first case, only oxygen was considered as the gasifying agent; in the second one, oxygen and steam were added to the reactor without steam leaving the gasifier being recycled back to the process; in the last case, besides oxygen, all steam leaving the gasifier was recycled back and used as a gasifying agent. The aim of the last case was to observe the gasifier operation when all the water leaving the gasifier is recycled back to the reactor. Steam leaving the gasifier includes unreacted introduced steam, steam from feed moisture and also steam produced in the gasifier by gasification reactions. Simulations were carried out for both samples; the different effects of these two feed compositions are highlighted.

Optimal OBR and SBR were estimated for every operating regime. The maximal value of MBR was the first condition for optimal OBR and SBR. In addition, temperature in the gasifier of at least 900 °C was also a necessary condition. High temperature in the gasifier ensures methane, light hydrocarbons and tar decomposition. When a maximum on the MBR versus OBR and SBR curves occurred at a temperature below 900 °C, the highest MBR meeting the condition for 900 °C was selected, and the corresponding values of OBR and SBR were considered as the optimal ones.

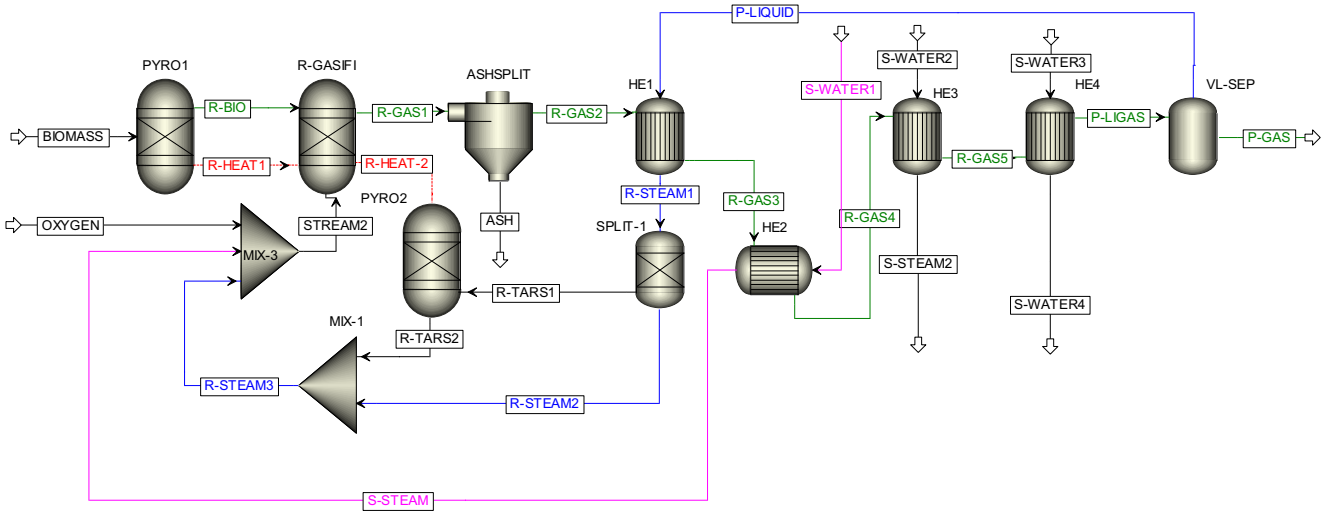

Fig. 2 Biomass gasification process flow diagram

4.1 Case 1: only oxygen as gasifying agent

Figure 3 shows the methanol to biomass ratio and gasifier adiabatic temperature at different OBR when only oxygen was used as the gasifying agent; here, it can be seen that both samples show a maximum MBR near OBR of 0.5. The reactor adiabatic temperature increases up to 2500 °C for the OBR value equal to 1.2. The maximum MBR was 0.31 and 0.32 for Sample 1 and Sample 2, respectively, at OBR of 0.48 and 0.49. However, the reactor adiabatic temperature at these conditions was only 701 °C and 715 °C, respectively, and the condition for reactor temperature (at least 900 °C) was not fulfilled. The OBR value meeting this condition for reactor temperature is 0.52 for Sample 1 and 0.54 for Sample 2. MBR at these conditions was 0.26 for Sample 1 and 0.29 for Sample 2.

4.2 Case 2: oxygen and steam as gasifying agents without steam recycling

If only oxygen is used as the gasifying agent, the H_2/CO ratio is too low and MBR is limited by the concentration of H_2 in the syngas. Figure 4 supports this claim. At optimal OBR, H_2/CO is only around 0.75 for Sample 1. This means that only a portion of CO can be used in the methanol synthesis because of H_2 unavailability. To increase the H_2 concentration in the syngas, steam is added to promote steam reforming and shift reactions. In this case, no recycle of the unreacted steam and tar was considered, but the condensate was separated from the product gas.

Figures 5 and 6 show MBR at different OBR and SBR for Sample 1 and Sample 2, respectively. Maximum MBR recorded for Sample 1 was 0.46 and for Sample 2 it was 0.49. These

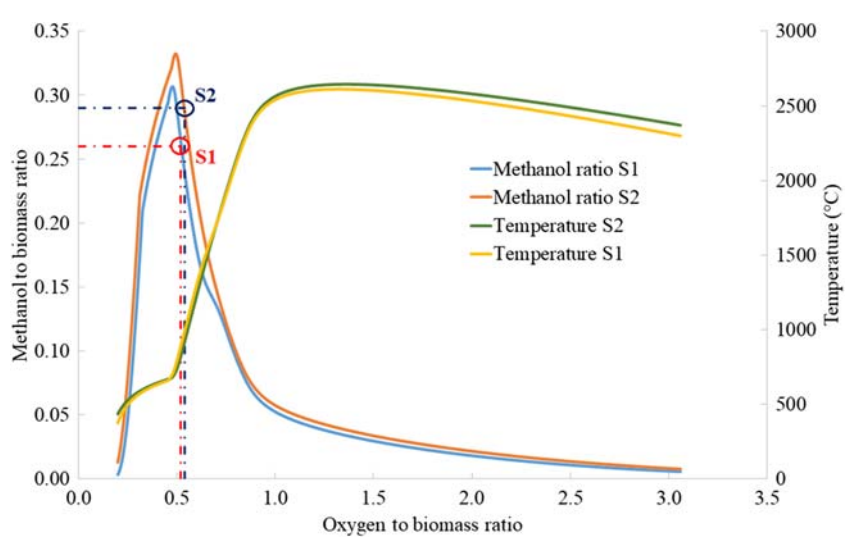

Fig. 3 Methanol to biomass ratio and gasifier temperature versus oxygen to biomass ratio

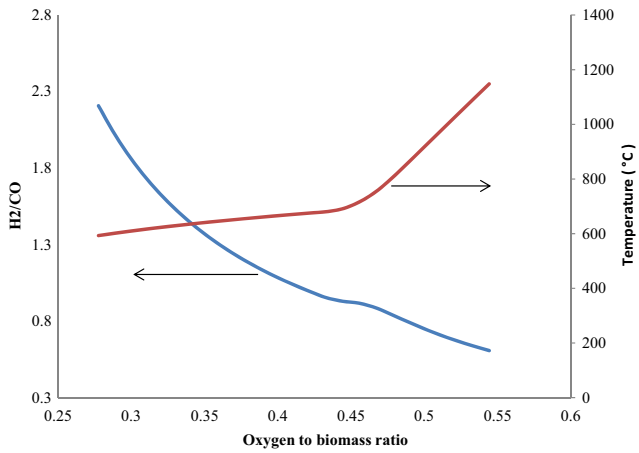

Fig. 4 H_2/CO ratio at different oxygen to biomass ratios and reactor temperatures for Sample 1

maximum values were reached at OBR of 0.48 and SBR of 0.42 for Sample 1 and at OBR of 0.48 and SBR of 0.51 for Sample 2. However, these maximum MBRs were reached at the rector temperature of 679 °C in case of Sample 1 and of 688 °C in case of Sample 2; therefore, the condition of reactor temperature equal to at least 900 °C was not fulfilled. At the gasifier temperature of 900 °C, OBR was 0.59 and SBR was 1.04 for Sample 1, and MBR was 0.41. For Sample 2, slightly higher MBR was reached (0.43), and the corresponding OBR was 0.57 and SBR was 0.89.

For optimal BMR search, the adjusted variable was SBR/OBR with the step change of 0.01, which is, however, too large and caused oscillatory behaviour of the depicted surface at higher SBR values (Figs. 5 and 6). To reduce the calculation time, two different values of the SBR/OBR step were used. First, using a step of 0.01 for the whole range of SBR/OBR values, MBRs were calculated and using a step of 0.0006 only for locations near the maximum MBR, a more exact value of optimal MBR was determined. Therefore, the optimal value of MBR is not affected by the oscillatory behaviour of surfaces seen in Figs. 5 and 6.

Lower moisture and ash content of Sample 2 resulted in higher MBR. Comparing the results of gasification with both oxygen and steam to the results achieved for Case 1 when only oxygen was used as the gasifying gent, it can be concluded that addition of steam increases the MBR by around 50%.

4.3 Case 3: oxygen and recycled steam as gasifying agents

Steam needed for reforming reactions in the gasifier can come from an external source or it can be produced inside the process from supply water (S-WATER1 stream in Fig. 2) or from water condensed in condensers when produced gas is cooled (P-LIQUID stream in Fig. 2). Recycling of condensed water and organic fraction has a number of advantages. Better process efficiency can be achieved by reducing carbon and hydrogen losses. In addition, the need for supply water can be reduced to minimum. If only a part of condensables is recycled, from the calculation point of view, the situation is similar as in Case 2. However, still, additional operations are required for water and tar disposal. Therefore, recycling of all condensed streams back to the gasifier is very attractive. Recycling the whole condensable part of the gas (tar and water) back to the gasifier can reduce the process cost as the number of operations required for tar and water disposal is significantly reduced. However, the question is the effect on the gasifier performance.

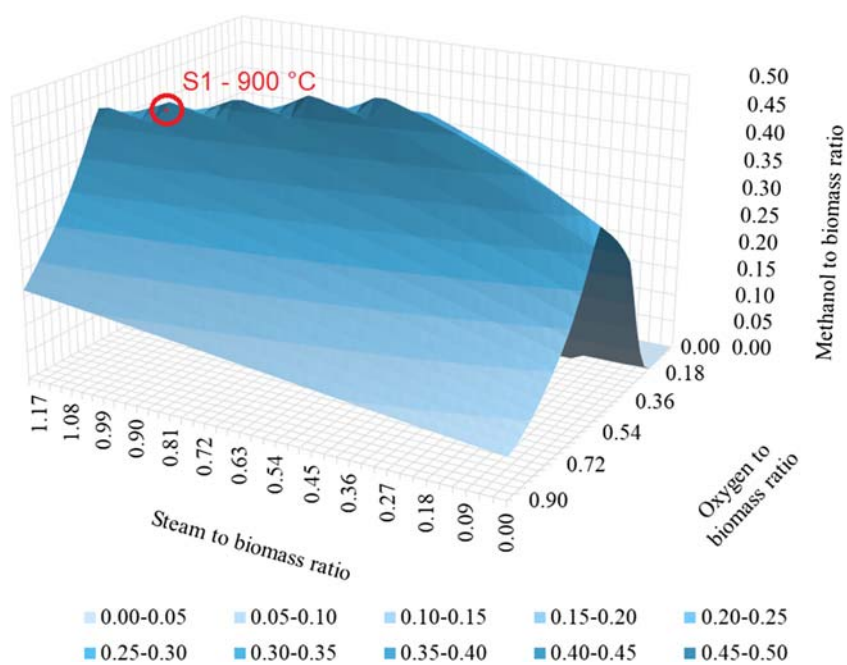

Fig. 5 Methanol to biomass ratio versus oxygen to biomass ratio and steam to biomass ratio for Sample 1

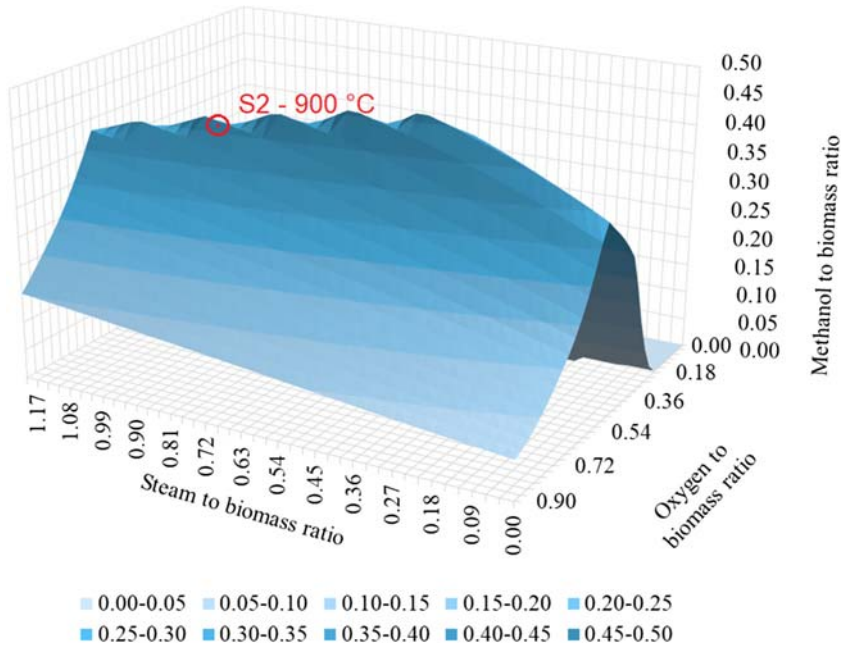

Fig. 6 Methanol to biomass ratio versus oxygen to biomass ratio and steam to biomass ratio for Sample 2

The aim of this experiment (Case 3) was to investigate a situation when all steam leaving the gasifier is recycled back to the gasifier as a gasifying agent together with oxygen. Steam leaving the gasifier comes from unreacted steam added to the reactor, moisture content of the feed and steam created by the chemical reactions. Therefore, the amount of steam leaving the gasifier depends on the feed composition, gasifier conditions and the amount of steam introduced to the reactor.

From the calculation point of view, it is an iterative calculation starting with a SBR value reached in the previous case. In the second iteration, the amount of water leaving the gasifier was used as the steam flow to the reactor. The default iterative method (Wegstein method) in Aspen Plus was used for tear stream convergence. The calculation converged always below 30 iterations. MBR and temperature are shown in Fig. 7 as a dependence on OBR for both samples.

For Sample 1, the maximum temperature was 810 °C. Thus, the required temperature of 900 °C was not reached. Maximum MBR was 0.43, and it was reached at OBR of 0.52 and SBR of 0.61. Temperature in the gasifier was 755.6 °C. For Sample 2, the gasifier temperature of 900 °C was reached and the MBR value of 0.39 and OBR of 0.62 and SBR of 1.412.

From this observation, it results that recycling of all steam leaving the gasifier depends on the feed composition. At high moisture content of feed and low heating value, large amounts of water should be recycled. By increasing the steam flow to the reactor, its temperature decreases; to reach the required reactor temperature, more oxygen has to be introduced. However, as it results also from Fig. 3, the reactor adiabatic temperature shows a maximum with the increasing OBR. Finally, before doing a decision on recycling all steam and

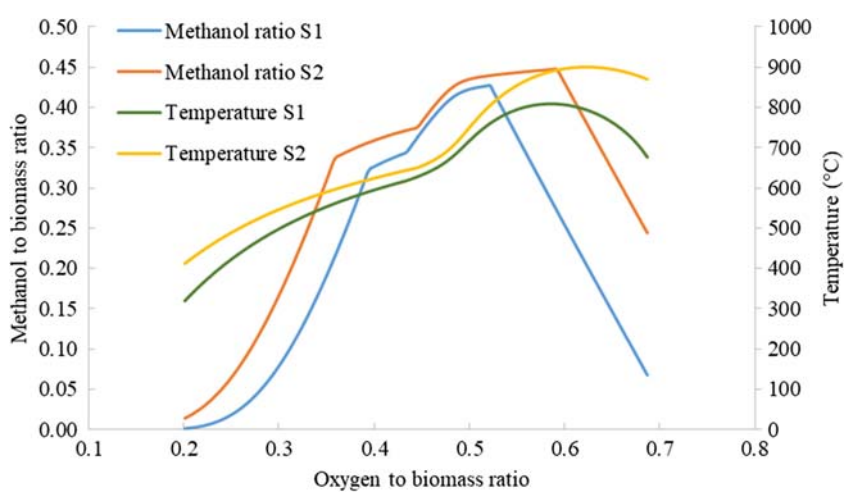

Fig. 7 Methanol to biomass ratio and temperature versus oxygen to biomass ratio

Table 3 Summary of results

Case	Biomass	MBR status	Temperature (°C)	OBR	SBR	MBR
Case 1	Sample 1	Maximal	701.4	0.48		0.31
	Sample 1	Optimal	903.1	0.52		0.26
	Sample 2	Maximal	715.5	0.48		0.33
	Sample 2	Optimal	904.8	0.57		0.29
Case 2	Sample 1	Maximal	678.9	0.48	0.42	0.46
	Sample 1	Optimal	900.1	0.59	1.04	0.41
	Sample 2	Maximal	688.2	0.48	0.51	0.49
	Sample 2	Optimal	900.1	0.57	0.89	0.43
Case 3	Sample 1	Maximal	755.6	0.52	0.61	0.43
	Sample 1	Optimal	–	–	–	–
	Sample 2	Maximal	896.3	0.60	1.21	0.43
	Sample 2	Optimal	900.0	0.62	1.41	0.39

tar leaving the reactor, its effect on the reactor temperature and H_2 and CO concentration should be studied.

A summary of the results of all three cases is presented in Table 3. The MBR status "Maximal" represents maximal reached MBR without meeting the requirement for reactor temperature, and "Optimal" represents maximal reached MBR when the reactor temperature condition is met.

5 Conclusion

Biomass to methanol process was studied using the Aspen simulation and experimental characterization of raw materials. Simulations were carried out for two samples of mixed agricultural waste in three different cases to find optimal oxygen to biomass ratio (OBR) and steam to biomass ratio (SBR) for the process. Optimal OBR was between 0.52 and 0.62 for all cases. The methanol to biomass ratio (MBR) increased by around 50% when steam was added to the process. Optimal steam to biomass ratio varied from 0.89 to 1.41. The highest MBR (0.43) at the reactor temperature of 900 °C was reached for Sample 2 and Case 2 when oxygen and steam were used as gasifying agents.

Optimal OBR is influenced also by the raw material composition. For Sample 1 with approximately 3% higher moisture content and 1% higher ash content compared with Sample 2, an increase of 11% in OBR was calculated. Composition of feed also has a crucial effect on the possibility of recycling all steam leaving the gasifier back to the system. If the feed is not dry enough or its calorific value is low, recycling of all steam can decrease the gasifier temperature. It can be stated that lower moisture and higher heating value of biomass lead to better methanol to biomass ratio (MBR).

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