

Waste Biomass to Methanol – Optimisation of the Gasification Agent to Feed Ratio

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Residues from agriculture and forest maintenance (lignocellulosic waste biomass) create a huge source of renewable energy and valuable materials. Gasification of biomass enables the production of combustible gases consisting mainly of H₂, CO, CO₂ and CH₄. Air, oxygen, steam or their mixtures can be used as gasifying agents. When air is used as a gasifying agent, N₂ is also present in the product gases. Gaseous product also contain small amounts of light hydrocarbons, tar and traces of H₂S, NH₃ and HCl. This gas can be used as syngas feed for methanol synthesis after treatment. The treatment steps include particles and tar removal, H₂S, NH₃ and HCl removal and reduction of CO₂ concentration. When synthesis gas is used for methanol production, concentration of H₂S has to be below 100 ppb, concentration of HCl below 1 ppb and concentration of NH₃ below 10 ppb (E4Tech, 2009). Product gas composition and tar content depend on waste composition, temperature in the gasifier and the type of gasification technology used.

One of the most important parameters with crucial effect on gas composition and reactor temperature is the oxidising agent to feed mass flow ratio. A mathematical model of the gasification process can provide an estimation of the optimal oxidising agent to feed ratio. The simplest gasification model considers a chemical equilibrium and its calculation based on the Gibbs free energy minimisation considering only thermodynamic limitations. This model disregards any reaction or transport rate mechanisms (Materazzi et al., 2013). However, the equilibrium model of gasification is reliable and in good agreement with the experiment measurements at the gasifier temperatures above 800 °C (Haydary, 2018).

In this work, gasification process of two samples of mixed agricultural waste and synthesis of methanol from the produced gas was designed and simulated in the Aspen Plus environment. Equilibrium model was applied. 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 and steam flows were optimised to achieve maximum theoretical yield of methanol while maintaining the temperature in the gasifier of at least 900 °C. Unreacted steam and produced tar were condensed and fed back to the gasifier to achieve better steam and tar conversion.

Materials and methods

Two samples of mixed agricultural waste biomass were studied. Composition of each sample is shown in Table 1. Table 2 shows the moisture and ash content, ultimate analysis and higher heating value (HHV) of both mixed samples. Parameters of the mixed samples were calculated based on parameters measured for individual components.

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 |

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 | |
| 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 |

Pure oxygen and steam were used as gasifying agents. The application of steam ensured increased H₂ yield and the use of pure oxygen led to low concentrations of N₂, CH₄ and tars in the product gas. Efficiency of the gasification process was determined by the the methanol to biomass ratio (MBR) calculated according to the following equations:

$$MBR = \frac{8 \cdot \dot{m}_{H_2}}{\dot{m}_{BIO}} \alpha \quad (1)$$

$$k_{CO} = \frac{\dot{m}_{CO}}{7 \cdot \dot{m}_{H_2}} \quad (2)$$

$$\text{if } k_{CO} \geq 1; \alpha = 1 \quad (3)$$

$$\text{if } k_{CO} < 1; \alpha = k_{CO} \quad (4)$$

Where \dot{m}_{H_2} represents the mass flow of H₂ in the gas leaving the gasification step, \dot{m}_{CO} the mass flow of CO and \dot{m}_{BIO} , the mass flow of feed biomass. Excess of CO is expressed by k_{CO} ; if $k_{CO} > 1$, variable $\alpha = 1$ because H₂ is the limiting reagent, if $k_{CO} < 1$, variable $\alpha = k_{CO}$ and CO is the limiting reagent.

Error! Reference source not found. 1 shows MBR versus oxygen to biomass ratio and steam to biomass ratio for both samples. Maximum MBR of 0.462 was reached at the oxygen to biomass ratio of 0.480 and the steam to biomass ratio of 0.420. However, the temperature in the gasifier was only 678.9 °C. Because temperature of at least 900 °C was set as a condition, the optimal oxygen to biomass ratio was estimated to be 0.591 and the steam to biomass ratio was 1.04. At these conditions, MBR decreased to 0.408. For Sample 2 at the gasification temperature 900 °C, the optimal oxygen to biomass ratio was 0.574 and the steam to biomass ratio was 0.889, MBR was 0.426.

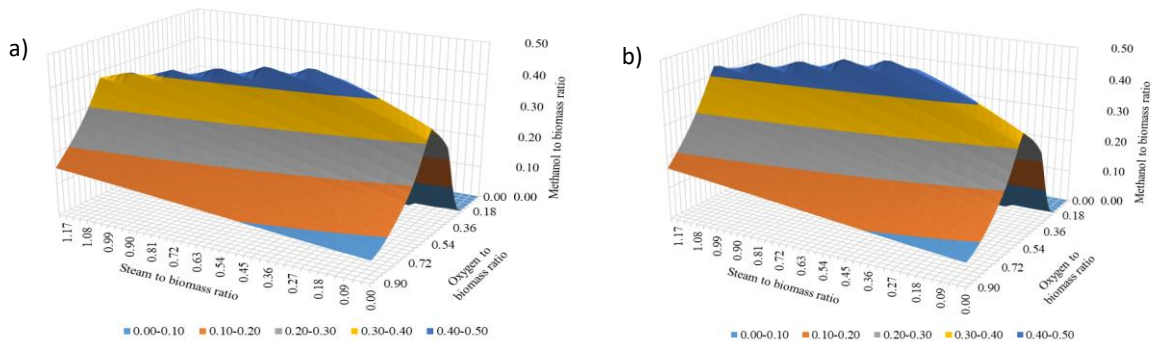


Figure 1. Methanol to biomass ratio versus the oxygen to biomass ratio and the steam to biomass ratio. a-Sample 1, b- Sample 2

Using recycled steam or supply steam with oxygen as the gasifying agent leads to higher MBR. It can be stated that lower moisture and higher heating value of biomass lead to better methanol to biomass ratio.

Acknowledgement

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References

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