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Biomass-derived oxymethylene ethers as diesel additives: A thermodynamic analysis

Xiaolei Zhang¹, Amit Kumar^{1,*}, Ulrich Arnold², Jörg Sauer²

¹Department of Mechanical Engineering, University of Alberta, Edmonton, Alberta T6G 2G8, Canada

²Institute of Catalysis Research and Technology (IKFT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Campus Nord, Karlsruhe Institute of Technology, Karlsruhe, Germany

Abstract

Conversion of biomass for production of liquid fuels can help in reducing the greenhouse gas (GHG) emissions which are predominantly generated by combustion of fossil fuels. Adding oxymethylene ethers (OMEs) in conventional diesel fuel has the potential to reduce soot formation during the combustion in a diesel engine. OMEs are downstream products of syngas, which can be generated by the gasification of biomass. In this research, a thermodynamic analysis has been conducted through development of data intensive process models of all the unit operations involved in production of OMEs from biomass. Based on the developed model, the key process parameters affecting the OMEs production including equivalence ratio, H₂/CO ratio, and extra water flow rate were identified. This was followed by development of an optimal process design for high OMEs production. It was found that for a fluidized bed gasifier with heat capacity of 28 MW, the conditions for highest OMEs production are at an air amount of 317 tonne/day, at H₂/CO ratio of 2.1, and without extra water injection. At this level, the total OMEs production is 55 tonne/day (13 tonne/day OME₃ and 9 tonne/day OME₄). This model would further be used in a techno-economic assessment study of the whole biomass conversion chain to determine the most attractive pathways.

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1. Introduction

As a CO₂-neutral and renewable energy resource, the utilization of biomass has the potential to reduce greenhouse gas (GHG) emissions. Production of liquid fuels from biomass is a promising technology. These biomass-derived liquid fuels can be blended with petroleum-based diesel, which can reduce the consumption of petroleum-based diesel and provide a solution for development of an environment

* Corresponding author. Tel.: +1-780-492-7797; fax: +1-780-492-2200.
E-mail address: Amit.Kumar@ualberta.ca.

friendly industry. Diesel engine is one of the most common internal combustion engines. Its exhaust contains air contaminants (NO_x and soot). Soot remains a significant problem during diesel combustion.

Adding biomass-based oxygenated compounds in diesel fuel can reduce soot formation during the diesel combustion [1]. The most frequently diesel additives discussed in literature are: dimethyl ether (DME), dimethoxymethane (DMM), and OMEs. Using of DME and DMM require engine modification because of increased vapor pressure [2, 3]. OMEs, with chemical structure CH₃-O-(CH₂-O)_n-CH₃, have higher viscosities, cetane number, and boiling points [4], and are acknowledged as the preferred diesel additives without changing the engine's infrastructure. Even though the OMEs production cost maybe higher compared to DME or DMM, but it could be attractive if all the cost components are considered including the engine modification cost.

Burger et al. [1] studied the OMEs formation process from methanol: formaldehyde (FA) is produced from methanol dehydrogenation, FA reacts with methanol to form DMM by heterogeneously catalyzed reactive distillation, DMM is OME_n with n=1, the other OMEs are produced by adding FA. The optimal OMEs chain length is n=3,4. The authors [5] also studied the OME formation from DMM and trioxane (TRI), with the chemical equilibrium well described.

Most of the previous studies focus on the OMEs production from methanol, however, very limited number of studies has focused on the systemic investigation of the OMEs production from biomass feedstock. The main purpose of this work is to build a systematic model on the whole process of production of OMEs from biomass; test key parameters that affect the process; and design an optimal process aiming at high OMEs (especially OME₃ and OME₄) production. The developed model would further be used in conducting a techno-economic assessment study to determine the best pathway forward for producing OMEs for blending it in petroleum based fuel to make it environmentally friendly.

2. Methodology

The model was developed using Aspen Plus. The feedstock is untreated wood chips, the detailed characteristics from ECN Phyllis classification are shown in Table 1.

Table 1. Characteristics of wood feedstock.

Proximate Analysis (wt %) (dry basis)				Ultimate Analysis (wt %) (dry basis)							LHV (as received)
Moisture	Fixed Carbon	Volatile Matter	Ash	Ash	C	H	N	Cl	S	O	
40.0	39.3	59.8	0.9	0.9	48.6	6	0.14	0.005	0.02	44.335	8.73 MJ/kg

The key steps of the model system are shown in Figure 1. The gasifier is a circulating fluidized bed (CFB) with the heat capacity of 28 MW using sand as a bed material. Empirical equations are used to calculate the yield of gas, tar, and solid char [6]. The pyrolysis gases include H₂O, CO₂, CO, H₂, some light hydrocarbons, and other gases. Tar compositions include C₆H₆, C₆H₆O, C₇H₈, and C₁₀H₈. It is assumed that 32% N, 46% S, and 28% Cl remain in the solid char. Char reacts with both O₂ and CO₂ during char gasification. Nickel-based, copper/zinc oxide/alumina, and Amberlyst 46 catalysts were used in the tar reforming, methanol production, and OME synthesis processes, respectively. The equilibrium constant for the OMEs synthesis in literature [5] was adopted.

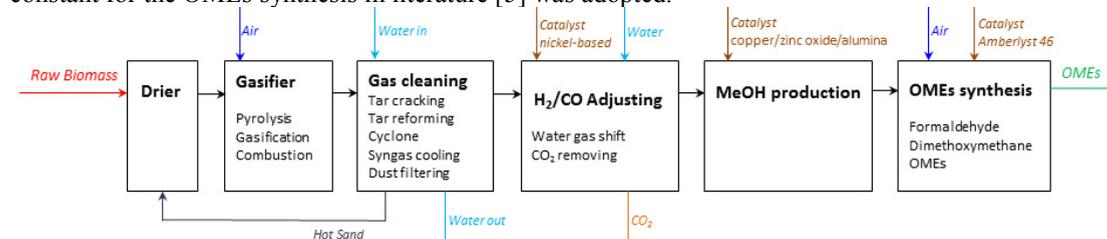


Fig. 1. Overview of the process model for OMEs production from biomass-derived syngas.

The model results were validated by comparing with the result from an earlier study performed [2] under the same conditions. TRI was used as a stable source of FA in reference [2]. The results are only slightly different on the FA or TRI mass fraction, which is allowable.

3. Results and discussion

3.1. Effect factors

The first important effect factor is equivalence ratio. Figure 2(a) shows the influence of equivalence ratio on the OMEs production. The equivalence ratio is defined as the stoichiometric air-fuel mass ratio divided by the actual air-fuel mass ratio. λ is the reciprocal of equivalence ratio. It can be seen that the OMEs production increase firstly and followed by decreasing as the air flow increases, when the actual air flow is 25% of stoichiometric air, the OMEs production becomes maximum. The reason is the OMEs production is affected by both gasification temperature and biomass gasified fraction, higher gasification temperature and higher gasification fraction lead to higher OMEs production. The temperature increases initially due to more combusted biomass, later the temperature starts decreasing slightly as the actual air flow increases, because more N_2 in air cools down the system. For gasification fraction, however, it decreases proportionally as the actual air increases. The model result shows that for a fixed feedstock flow rate (3.21 kg/s), the stoichiometric air flow is 14.83 kg/s, the optimal air flow is 3.67 kg/s.

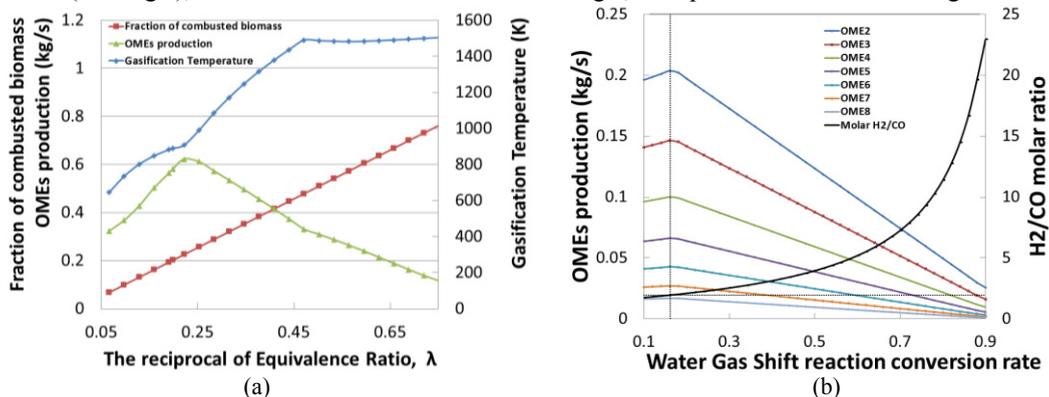


Fig. 2. Effect factors on the OMEs production in the case of this model. (a) Equivalence ratio; (b) H_2/CO molar ratio.

Another important effect factor is H_2/CO ratio before the methanol synthesis process. As shown in Figure 2(b), The OMEs production is maximum when the H_2/CO molar ratio at 2.1.

Moreover, some extra water may be needed for steam reforming and water gas shift reaction. For the present case, no extra water is needed since the moisture content in the feedstock provides enough steam.

3.2. An optimal process design

Based on the previous analysis, an optimal process for producing OMEs from biomass was designed. The feedstock is wood chips with 3.21 kg/s flow rate, the gasifier is CFB with sand as bed material. The gasification process is energy self-sufficient by partial biomass combustion. The flow rates of the whole process are shown in Figure 3. For the highest OMEs production, the optimal air is 3.67 kg/s. The H_2/CO ratio for raw syngas is 0.96, after adjusting the syngas, the ratio becomes 2.1. 1.15 kg/s methanol was produced, and followed by 0.64 kg/s OMEs (0.155 kg/s of OME₃ and 0.106kg/s of OME₄).

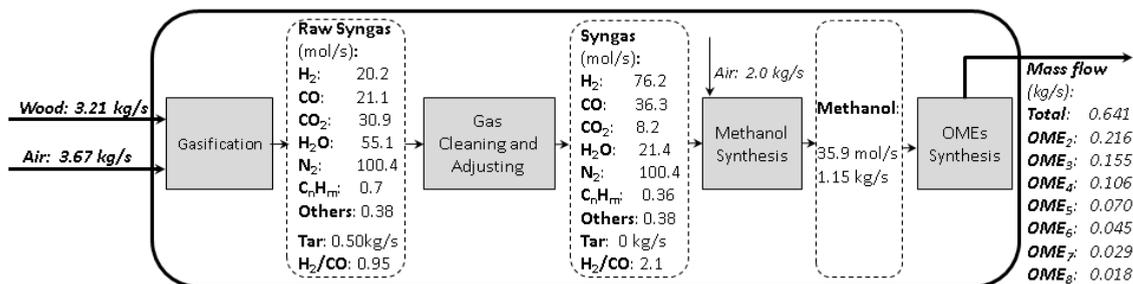


Fig. 3. The mass flow in the designed process. The C_nH_m in the gas composition include CH_4 , C_2H_4 , C_2H_6 ; Others include NH_3 , H_2S , HCL , SO_2 , NO , N_2O , CHN ; And tar include C_6H_6 , C_6H_6O , C_7H_8 , $C_{10}H_8$

4. Conclusions

Because of the physical properties, OMEs may be preferred future diesel additives over DME and DMM, a systematic model for the whole process of OMEs formation from biomass was built in this research. A circulating fluidized bed with hot sand as bed material was chosen as the gasifier, the raw syngas is cleaned and adjusted to a suitable H_2/CO ratio, followed by synthesis of methanol and OMEs.

Different air flow rate, H_2/CO ratio, and extra water were tested based on the built model, for 277 tonne/day wood chips, the condition with optimal air flow 317 tonne/day, yields the highest products. The production of OMEs is 55 tonne/day with 13 tonne/day OME₃ and 9 tonne/day OME₄.

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Biography

Xiaolei Zhang is a Post-doctoral Fellow in Dr. Kumar's group in Department of Mechanical Engineering at University of Alberta, Canada. She is working on Techno-Economic analysis of Renewable energy systems. Currently, her research focus on oxymethylene ethers production from biomass gasification derived syngas.