CO_2 gasification of microalgae (*N. Oculata*) – A thermodynamic study

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Abstract. A new model of CO_2 gasification has been developed in the Aspen Plus. The potential of microalgae (*N. oculata)* for CO_2 gasification also has been investigated. The present gasification process utilizes the CO_2 at atmospheric pressure as the gasifying agent. The steam is also injected to the gasification to enhance the H_2 production. The composition of the producer gas and gasification system efficiency (GSE) are used for performance evaluation. It is found that the CO_2 gasification of microalgae produces a producer gas with a high concentration of CO and H_2. The GSE indicates that the process works at high performance.

1 Introduction

The increase of the fossil fuel consumption during the last decades causes a global warming. The renewable fuel has been considered as a potential solution of the corresponding problem. Among the available renewable resources, biomass is considered as a potential alternative resources with minimum negative impact due to its ability to reduce the CO_2 from the atmosphere and its low sulfur content [1].

Gasification is a potential biomass conversion process since it produces a producer gas which mainly consists of H_2, CO, CO_2 and CH_4 [2]. The gasifying agent has a considerable effect on the producer gas composition. [3], [4] and [5, 6] reported the injection of steam to the gasifier enhanced the H_2 production in the producer gas. The use of CO_2 as a gasifying agent attracts the attention of some researchers. For instance, [7] investigated the gasification of pine sawdust using CO_2 over Ni/Al precipitation catalyst. [8] studied the gasification of beech sawdust in the entrained flow reactor. [9] developed a model to investigate the performance of biomass gasification with CO_2 using fluidized bed gasifier. Recently, some research have focused on microalgae cultivation and processing because it offers positive environmental impacts [10-12]. To the best of our knowledge, only one literature discussing the CO_2 gasification of algae. [13] carried out CO_2 gasification of microalgae char using high-pressure thermogravimetric analyzer (HP-TGA).

2 Methodology

The minimization of Gibbs free energy is used for thermodynamic modeling of gasification process which involves solid, liquid and gas phases [14]. The process flow diagram of the gasification system can be seen in Fig. 1. The biomass and the gasifying agents (CO_2 and H_2O) are fed to the gasifier separately. It is worth noting that the gasifier is modelled using two blocks: the DECOM block (RYield) and the Reduction block (RGibbs). A Fortran code is embedded in the DECOM block to convert the microalgae feed stock (non-conventional component) into conventional components. While the gasification reactions occur based on the method of Minimization of Gibbs Free Energy in the Reduction block. It is worth mentioning that during gasification process the following consecutive reactions occur in the gasifier:

Boudouard reaction	$C + CO_2 \leftrightarrow 2CO \quad \Delta H^0_{298} = +172$ MJ/kmol	(1)
Steam reforming	$C + H_2O \leftrightarrow CO + H_2 \quad \Delta H^0_{298} = +131$ MJ/kmol	(2)
Methane formation	$C + 2H_2 \leftrightarrow CH_4 \quad \Delta H^0_{298} = -74$MJ/kmol	(3)
Water-gas shift reaction	$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^0_{298} = -42$ MJ/kmol	(4)
Methane reforming	$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H^0_{298} = +206$ MJ/kmol	(5)
CO_2 reforming	$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad \Delta H^0_{298} = +247$ MJ/kmol	(6)

The gasification products flow to the cyclone to separate the gaseous products (H_2, CO, H_2O, and CO_2) and solid products (ash and unconverted char). The gaseous products are fed to the reformer. The reformer products is sent to the CO_2 absorber to capture the CO_2 in the reformer products. The pure CO_2 from the absorber is then cooled and compressed to 523 K and 80 bar, respectively. The producer gas is expanded and cooled to 3 bar and 298 K, respectively. The ultimate and proximate analysis of the biomass, including the heating value of biomass are summarized in Table 1. The operating conditions of the gasification process are summarized in Table 2.

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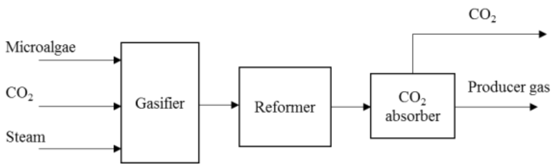

Fig. 1. Block diagram of the gasification process.

The performance of the gasification is evaluated in term of the dry composition of producer gas and gasification system efficiency (GSE) (Eq. (7)). One should note that the energy required for CO_2 absorption using amine is 3 MJ/kg CO_2 absorbed [15].

$$GSE = \frac{m_{pg} \times LHV_{pg} + E_{gen}}{m_{ma} \times LHV_{ma} + E_{req}} \quad (7)$$

Where m and LHV are mass flowrate and low heating value, respectively, while subscript pg and ma refer to the producer gas and the microalgae, respectively. The E_{gen} represents the total energy generated from the process while the E_{req} represents the total energy consumed by the process.

Table 1. Proximate and ultimate analysis of microalgae.

	Microalgae (*N. oculata*) [11]
Proximate (wt.%)	
Moisture	6.71
Volatile matters	78.94
Fixed carbon	7.95
Ash	6.4
Ultimate analysis (wt.%)	
C	47.50
H	6.15
O	46.35
N	n.r
S	n.r
Cl	n.r
High heating value (MJ/kg)	15.07

n.r : not reported

Table 2. Operating conditions in the simulation.

Inlet temperature of biomass, boiler feed water, and CO_2	25^{o}C
Temperature of steam entering gasifier	327^{o}C
Temperature of gasifier	70^{o}C
Temperature of reformer	800^{o}C
Pressure in the all blocks	2000 kPa
Stream class	MIXCINC
Thermodynamic package	Peng-Robinson

It is worth noticing that the model validation of the gasification block is conducted using the same feedstock and operating conditions with the ones employed by [16]. The composition of the producer gas from the gasifier is used as the baseline for model validation. It is clearly shown in Table 3 that the results of our simulation agree closely with the results reported by other author [16]. Indeed the relative error for H_2 and CO as the major producer gas component was less than 10%.

Table 3. Model validation. (Biomass $CH_{1.4}O_{0.6}$, CO_2/C = 0.5, T = 800 ^{o}C and P = 1 atm).

	Our simulation	Chaiwatanodom [16]	%Error
H_2	30.45%	30.98 %	1.75%
CO	63.13%	59.78 %	5.31%
CO_2	6.04%	9.01 %	n.r
CH_4	0.38%	4.30 %	n.r

3 Results and discussion

A microalgae feedstock with mass flow rate equal to 100 kg/h is fed to the gasifier. In addition, a CO_2 and a steam with mass flow rate of 151 kg/h, and 62 kg/h, respectively, are selected as the gasifying agents. It is worth noticing that the gasification system consists of the gasifier, the reformer and the CO_2 absorber, as shown in Fig. 1.

It is clearly shown in Fig. 2a that the microalgae disappears while the amount of H_2, CO, CO_2, and CH_4 significantly increase in the product stream of the gasifier. This indicates that the main task of the gasifier is the conversion of the solid feed stock (e.g., microalgae) into the gaseous products (H_2, CO, CO_2, CH_4 and H_2O) with the help of the gasifying agents (H_2O and CO_2). The decrease of the amount of microalgae and H_2O indicates that the microalgae is decomposed into gaseous products through steam reforming reaction (Eq. (2)). This is also confirmed by the increase of the CO and H_2 in the gasifier product. One should notice that the methane formation reaction (Eq. (3)) also takes place during CO_2 gasification of microalgae since the CH_4 presents in the gasifier product. When one look at Fig. 2a, the amount of CO_2 in the gasifier products is higher than that of in the gasifier feed. This indicates that water-gas shift reaction (Eq. (4)) occurs in the gasifier. Indeed, this also can be attributed to the decrease of the H_2O amount in the gasifier product.

In the reformer unit, the gasifier products is further reacted to produce higher concentration of combustible gases (CO and H_2). Fig. 2b indicates that the amount of CO_2 and CH_4 in the reformer feed stream are higher than their counterparts in the reformer product stream. This can be attributed to the methane reforming reaction (Eq. (5)) and CO_2 reforming reaction (Eq. (6)). This is confirmed by the increase of the amount of CO and H_2 in the stream of the reformer product.

The amounts of the components in the feed of CO_2 absorber and in the producer gas stream are depicted in Fig. 2c. The amount of the CO_2 in the producer gas stream is lower than its counterpart in the stream of

CO_2 absorber feed. This indicates that the CO_2 absorber significantly reduces the amount of non-combustible gas in the producer gas stream. It is worth mentioning that the producer gas consists of 45% H_2, 45% CO, 6% CO_2 and 4% CH_4 (dry basis), while the GSE of the process is 68%.

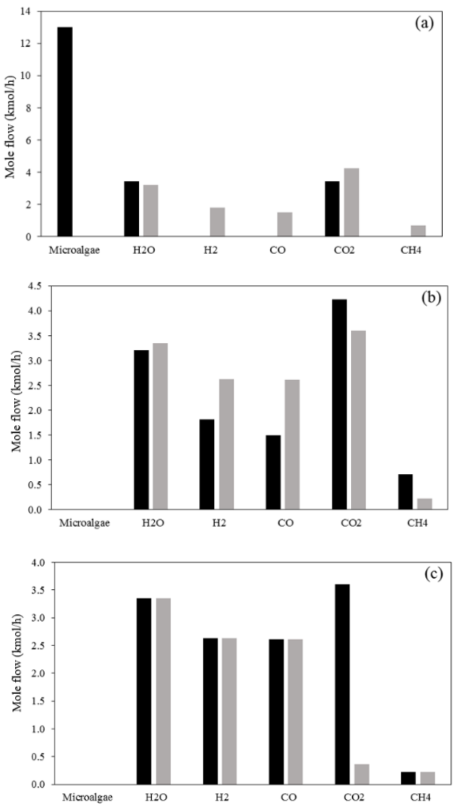

Fig. 2. Mole flow of the feed and product of (a) the gasifier, (b) the reformer, and (c) the CO_2 absorber. (feed: black; product: grey)

4 Conclusion

The production of producer gas with a high concentration of CO and H_2 via the CO_2 gasification of microalgae is simulated using Aspen Plus. The results show that the CO_2 gasification of microalgae can provide the producer gas with a high concentration of H_2 and CO. It is also reported that the GSE of the process is relatively high. In addition, high purity of CO_2 is also produced as the side-product of the process. Although the present model is developed only for the purpose of the preliminary study of the CO_2 gasification of algae. The results indicate that the CO_2 gasification of algae can potentially be a promising alternative of green technology with further optimization.

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