Improvement of integrated tar reformer with biomass gasification on produced H_2, tar removal and self heat sufficient: Thermodynamic analysis.

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Abstract

Integrated tar reformer with biomass gasification system on heat analysis and H_2 rich gas was investigated. This study was calculated under thermodynamic equilibrium of reactions. Tar was represented by toluene, phenol, naphthalene and pyrene, composition related with temperature. Gasification operating parameter, temperature at 973 K and oxygen: biomass ratio at 1/3 show high performance for produced hydrogen and low exothermic energy. When increasing operating tar reformer temperature, H_2 yield rises and tar composition near zero. But the tar reformer temperature increases higher ~800 K, unfortunately pyrene formation has come significant. Tar formation can reduce by increase steam into the tar reformer. Consequently, adding steam to tar reformer will increase required energy of integrated tar reformer with biomass gasification system. The operating parameter will be considered for higher H_2 and self supply energy.

Keywords: biomass gasification, tar reformer, produced H_2 and self supply energy.

1. Introduction

The renewable energy has been considerable in fossil fuel crisis and environment concern. Biofuels as well as renewable energy source are widely studied in biogas, biomass, bioethanol and biodiesel. The most of biofuels production still retain the biomass residue, so consideration on biomass to energy is magnitude for improved overall efficiency of biofuels. Gasification technology applies usually to convert biomass to fuel gas. Biomass gasifier produces H_2 and CO (syngas) used for produce electricity by generator or fuel cells. But the major problem of biomass gasification is tar (high molecular weight hydrocarbons) [1-7].

Tar in fuel gases condense at low temperature, and lead to clog and block in pipe lines, valves, filters, engines and cell stacks. Tar were removed by physical process, and reduced by thermal or catalytic reformer. Tar can reduce by increase gasifier temperature [2-5]. The catalytic tar reformer was studied in types of catalyst and operating condition [1, 6]. Many tar kinetics on catalyst were reviewed by C. Li and K. Suzuki, 2009 [1], but first-order reaction approach not good enough to explain tar reformer. J. Li *et al.* (2008) studied to develop novel nano-NiO (12-18 nm) on γ-Al2O3 for reforming tar [6]. The tar reformer efficiency is nearly 100%, at 800°C and 12 wt %. Exceptionally, benzene, toluene and cyclic hydrocarbon compound were used as tar destruction model compound for study experiment tar reforming catalyst [7-8]. C. Li. *et al.* (2010) studied Ni/MgO/CaO on toluene steam reforming [7]. This catalyst showed outstanding activity of toluene steam reforming. Benzene steam reforming over various Ni supported metal oxide catalysts was studied [8]. Ni/CeO_2(75%)-ZrO_2(25%) catalyst was shown activity higher than commercial Ni catalyst. T. Furusawa and A. Tsutsumi (2005) studied performances of Co/MgO catalysts for the tar steam reforming by used naphthalene as a model compound of tar [9]. Theoretical analysis of tar reformer was considered by D. Singh *et al.* (2005) [2], tar reforming on carbon deposition in anode SOFC. D. Xu *et al.* (2009) [10] studied in supercritical steam gasification on Na_2CO_3 catalytic reformer of glycine and glycerol, used as tar model. Gasifier efficiency on 0.1 wt% Na_2CO_3 can be increased up to 95.8% and 98%, and hydrogen yield to 4.14 and 5.08 mol mol^{-1}, respectively. In-situ steam reforming in biomass gasification was investigated on tar decomposition and coke formation on mesoporous alumina catalyst [11]. Mesoporous alumina particle would form coke about 10-20%, but it still can convert tar component to syngas. A. Haryanto *et al.* (2009) studied on upgrade syngas form biomass gasification by various operating temperature and pressure and carbon : steam ratio. The hydrogen was increased 0.5-1.25 times of ordinary system, at 900-1100 K and 1-3 atm [12].

The operated tar reformer usually added external heat source for reforming reaction (endothermic reaction). But the gasification is generally exothermic reaction. Accordingly, association of biomass gasification system with tar reformer system (include steam and air system) was sufficient operated energy for reducing tar by not added external heat source. The significance parameters were amount of air : biomass ratio, steam : biomass, operation temperature.

This study, biomass gasification was investigated on suitable operating temperature; both of gasifier and tar reformer. And volume of air and steam was considered for self supply energy and high produced H_2. Thermodynamic equilibrium was used for calculated composition form chemical reactions.

2. Theory

Biomass gasification

Gasification technology produced syngas form hydro-carbon compound source, such as coal, wood and MSW. Biomass gasification was considered as well as renewable energy source. Biomass reacted with partial oxidation by air to syngas (Eq.1).

$$Biomass(with\ \ moisture) + Air \longrightarrow Syngas + Tar + Ash + ... \quad (1)$$

Furthermore syngas, tar and ash were byproduct of biomass gasification. The reduction of tar can use steam reformer, syngas will be increased by Eq.2

$$Tar + H_2O \longleftrightarrow CO + H_2 + CH_4 + CO_2 \quad (2)$$

The Schematic of biomass gasification incorporated with tar steam reformer illustrate Fig. 1. Downdraft biomass gasification and tar reformer were considered in term of high produced hydrogen and self supply energy (Eq. 3).

$$H_{gasification} + H_{reform} + H_{steam} + H_{air} \leq 0 \quad (3)$$

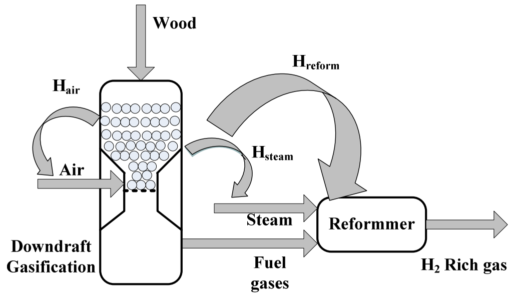

Fig. 1 Scheme of integrated tar reformer gasification system.

The tar compositions were investigated and listed by J. Gill et al. (1999) [12] on wood gasification by various operating temperature 700-900 °C. D. Singh et al. (2005) [2] used toluene (C_7H_8): represent all the one-ring compounds, naphthalene ($C_{10}H_8$): represent two-rings compounds, phenol (C_6H_6O): represent phenolic and other heterocyclic compounds and pyrene ($C_{16}H_{10}$): representing three-rings and higher compounds for reduced parameters of tar reforming. These results were analyzed for assumed compositions of tar, Fig. 2. This results use for example of tar composition on biomass gasification. Overall reaction of biomass gasification show in Eq. 4.

$$CH_xO_y + wH_2O + mO_2 \longleftrightarrow n_1H_2 + n_2CO + n_3CO_2 + n_4H_2O + n_5CH_4 \quad (4)$$

This work, wood use for represent biomass. The wood properties give details in Table 1. The chemical formula of wood is $CH_{1.79}O_{0.83}$ (neglect N=~$1.3x10^{-3}$).

Table 1. Wood properties analysis

Proximate Analysis	
Volatile Matter	74.76 %wt
Fixed Carbon	13.66 %wt
Ash	4.38 %wt
Moisture Content	5.41 %wt
High Heating Value	18.87 MJ/kg
Ultimate Analysis	
Carbon, C	44.24 %wt
Hydrogen, H	6.548 %wt
Nitrogen, N	0.071 %wt
Oxygen, O	49.141 %wt

Tar steam reforming

Represented tar is composed toluene, naphthalene, phenol and pyrene. The tar steam reforming (TSR), methane steam reforming (MSR) and water gas-shift reaction (WGSR) were considered (Eq. 5-10).

$$C_7H_8 + 7H_2O \longleftrightarrow 7CO + 11H_2 \quad (5)$$

$$C_{10}H_8 + 10H_2O \longleftrightarrow 10CO + 14H_2 \quad (6)$$

$$C_{16}H_{10} + 16H_2O \longleftrightarrow 16CO + 21H_2 \quad (7)$$

$$C_6H_6O + 5H_2O \longleftrightarrow 6CO + 8H_2 \quad (8)$$

$$CH_4 + H_2O \longleftrightarrow CO + 3H_2 \quad (9)$$

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \quad (10)$$

Heat of tar reformer (H_{reform}) calculated by summation of formation heat Eq.5-10.

For this paper, the thermodynamic analysis was done by calculating the equilibrium compositions using the free energy minimization.

3. Results and discussions

Biomass gasifier was operated by fed wood 1 kg hr^{-1}, operating temperature 873-1173 K, oxygen:biomass ratio ~0.33 –

~0.48 by mole, without added steam. Tar formation calculated by mass balance with results of Fig. 2. The results show that in Fig. 3. Produced hydrogen was improved by increase gasification temperature (T_{gs}). However gasification temperature higher than 973 K, the hydrogen performance will be dropped. At higher temperature, WGSR, exothermic reaction, will be less active than lower temperature. As a result, hydrogen yield decreased. Accordingly, increasing oxygen:biomass ratio (O_2:*BM*) was resulted reduced hydrogen too. Because of high oxygen concentration leads to combustion reaction, substitute partial oxidation with biomass. Appropriate conditions of gasifier are T_{gc} 973K and O_2:*BM* 0.33 for high produced hydrogen. Fig. 4 illustrates composition output gas and exothermic heat form biomass gasification. The results show clearly that oxygen react with biomass by combustion at high O_2:*BM* ratio. Carbon dioxide and water was raised by increasing oxygen, contrary of carbon monoxide and hydrogen. The exothermic energy increased at higher O_2:*BM* ratio.

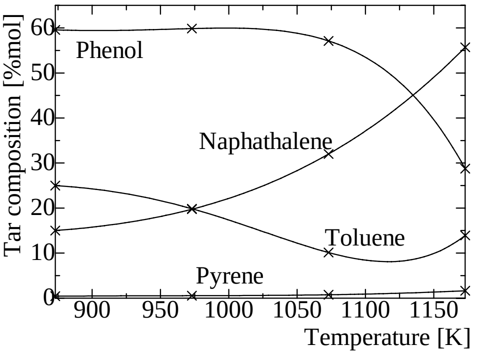

Fig. 2 Tars composition on operation temperature of gasification.

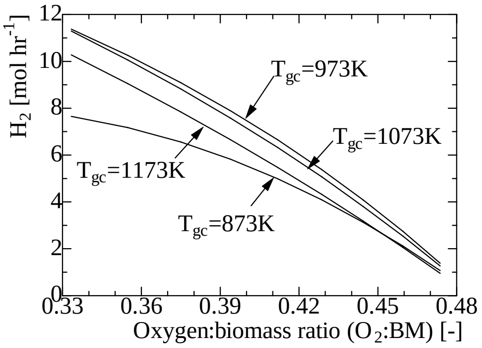

Fig. 3 Effect of operating gasification temperature (T_{gc}) and oxygen:biomass ratio (O_2:BM) on produced H_2.

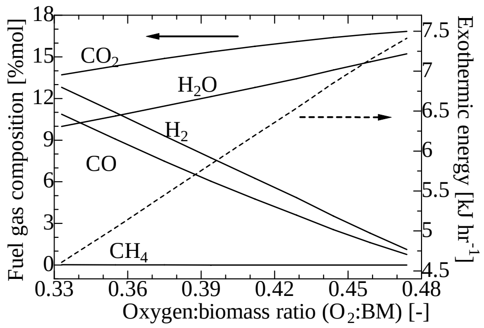

Fig. 4 Composition of fuel gases and exothermic energy on oxygen:bio-mass ratio (O_2:BM) (at T_{gc}= 973 K)

Tar steam reformer (Eq. 5-10) was considered for reduce/remove tar from fuel gas. Investigated parameters composed of operating reformer temperature (T_{rf}) 673-973 K and steam:biomass ratio (*S:BM*) ~0-3, at *S:BM* 0.5, T_{gc} 973 K and O_2:*BM* 1/3. Reformed gas compositions and tar composition on various temperatures show in Fig. 5. Syngas was rise when reformer temperature goes up, and the representing tar was completely eliminated at T_{rf} < 850 K. At higher temperature, pyrene formation is occurred. Additional, pyrene was increased by increasing reformer temperature. It is possible that steam lower than tar reformer required. Consequently, steam:biomass ratio was investigated (*S:BM* 0-3). The effect of *S:BM* illustrate in Fig. 6, at reformer temperature higher than 850 K. Increasing steam to reformer and temperature can increase syngas. At *S:BM* higher 1, increasing CO is not significant. Fig. 7 show energy analysis of integrated tar reformer with biomass gasification and tar formation. At *S:BM* =1, tar was not found in fuel gas. For self supply heat, reformer temperature 873, 923 and 973 K can operated with maximum *S:BM* about ~1.8, ~1.4 and ~1.2, respectively.

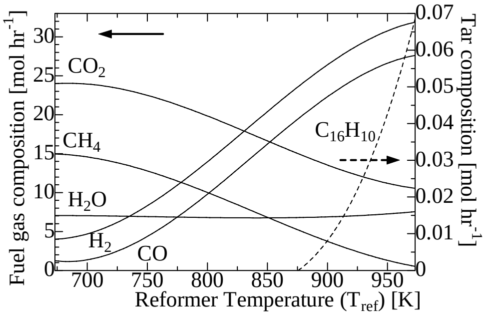

Fig. 5 Performance of reformer on operating temperatures (at O_2:*BM* ratio = 1/3, *S:BM* ratio = 0.5 and T_{gc}= 973 K)

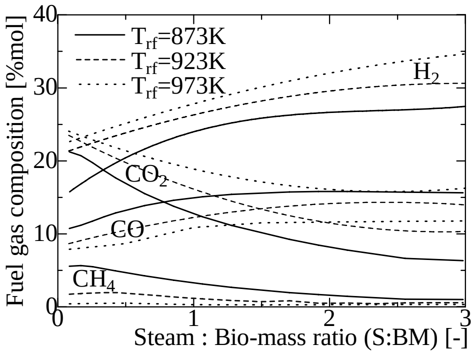

Fig. 6 Effect of steam:bio-mass ratio (*S:BM*) [-] and reforming temperature [K] on fuel gas composition [%mol] (at O_2*:BM* ratio = 1/3, T_{gc}=973 K).

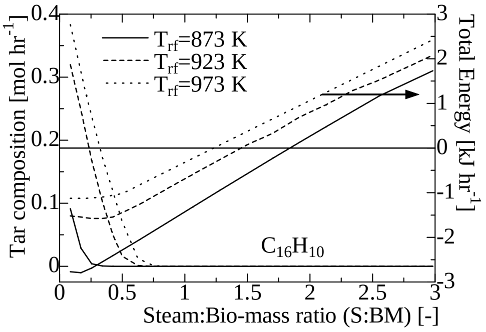

Fig. 7 Tar composition [%mol] and total energy [MJ hr^{-1}] on reforming temperature (T_{rf}) and steam:bio-mass ratio (*S:BM*) [-] (at O_2*:BM* ratio = 1/3, T_{gc}=973 K)

4. Conclusion

The integrated tar reformer with biomass gasification was investigated for improved performance of syngas producer, higher efficiency and environment friendly. This paper was studied by used wood as biomass source. Produced syngas depend on gasifier temperature, increased syngas by increasing temperature and decreasing O_2*:BM* (~0.33). But at higher than 973 K, produced syngas was down. Tar was represented by toluene, phenol, naphthalene and pyrene, modeled tar was guess by the result data. Performance of tar reformer depend on *S:BM* and T_{rf}. At *S:BM* over than 1, tar was eliminated by steam reforming reaction. Moreover, integrated tar reformer with biomass gasification can operate with self supply heat by themselves.

5. Acknowledgement

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Nomenclature

H_i	Heat of equipment i [kJ hr^{-1}]
TSR	Tar steam reforming
MSR	Methane steam reforming
WGSR	Water-gas shift reaction
T_{gc}	Gasifier temperature [K]
O_2:*BM*	Oxygen to biomass mole ratio[-]
S:BM	Steam to biomass mole ratio [-]
T_{rf}	Tar reformer temperature [K]