

BIOMASS GASIFICATION: ISSUES RELATED TO GAS CLEANING AND GAS TREATMENT

NAVNEET PATHAK^{a1}, DIBYENDU ROY^b AND SUDIP GHOSH^c

^{abc}Department of Mechanical Engineering, Indian Institute of Engineering Science and Technology, Shibpur, Howrah, India

ABSTRACT

Biomass gasification is a thermochemical process where solid biomass is converted into a combustible producer gas, while the gas is rich in combustible species like CO, CH₄ and H₂. This gas also contains some amount of tar and particulates. The formation of the tar is a critical problem that hinders large scale application of gasification technique. In conventional cleaning process the tar compounds are separated from the gas and in the process the heat value of gas reduced considerably. Instead of removing the tar compounds if it can be converted into usable combustible gas species, the efficiency of the system would increase. In this study, biomass gasification derived typical tar compounds namely toluene, benzene, and naphthalene have been thermally cracked. Reaction models for cracking of the tar compounds in the presence of the H₂ and steam have been developed and analyzed. The results suggested that the tar compounds could be effectively converted into combustible gas species under appropriate condition, particularly at high temperature.

KEYWORDS: Biomass Gasification, Gas Cleaning Process, Tar, Thermal Cracking.

Present energy resources are not sufficient for serving the demand of energy for a long time in future. Due to rapid growth of population the energy demand is increasing continuously. Fossil fuels have provided us cheap and convenient mode of energy for electric power generation purpose. Those have been also widely used as transportation fuels and for chemical production as well. Fossil fuels are non-renewable sources which are depleting rapidly due to its extensive use. Moreover, their massive utilization has also caused many problems such as environmental damage (e.g., ozone depletion, global warming) associated with various emissions. Changes in the energy supply structure are necessary to meet the growing energy demand. Thus world is moving towards other energy resources like solar power, wind energy, biomass, tidal energy, ocean energy, geothermal energy etc. which are renewable in nature [1]. These are more eco-friendly as compared to conventional fossil energy resources. They have a potential to serve our demand of energy for a prolong period [2], [3].

Biomass is one of the most underrated energy sources whose potential has not been widely used. It includes a wide range of material like forestry wastes, agricultural residues, kitchen waste, municipal waste, aquatic plant. It mostly comprises carbon, hydrogen, oxygen, nitrogen, sulphur, and some amount of alkali metals.

Biomass gasification is widely used for liquid and gas fuel production. This thermochemical process is used to convert biomass into H₂, CO, and CH₄ gas species [4], [5]. These combustible gases can be further utilised for electricity generation and other applications. During biomass gasification, the first process which takes place is pyrolysis. In this process

volatile and char are produced. The volatile and char are then combined with oxygen to form CO₂ and CO. At the end of gasification the char reacts with CO₂ in the presence of gasification agents like oxygen, steam, air to finally produce H₂ & CO mainly [4].

CO, CO₂, H₂, CH₄, H₂O, N₂ and some organic and inorganic compounds are the major constitute of producer gas produced in biomass gasification process [3], [6], [7]. It also contains some low and high molecular mass hydrocarbon compounds. Lower molecular mass hydrocarbon does not possess any threat and can be used as fuel. But higher molecular mass hydrocarbon acts as hindrance during application of producer gas. These higher molecular mass hydrocarbons are known as tar.

During biomass gasification process, tar compounds are formed as a by-product of gasification reaction. When producer gas is used in power production devices, tar compounds can cause major problems such as blocking, corrosion and erosion of equipment [7], [8].

In this study, several techniques and processes are discussed which are used to remove and convert tar into useful fuel gas components. Also, an equilibrium model has been developed for detailed study of thermal cracking of three typical biomass gasification derived tar compounds namely toluene, benzene and naphthalene in the presence of steam and hydrogen. The effects of different operating conditions like temperature and steam to carbon (S/C) ratio on the composition of product gas mixture during thermal cracking are also presented in this work.

TAR AND ITS TREATMENT

Tar is a mixture of aromatic compounds having high molecular mass which includes benzene, toluene represent one-ring hydrocarbons, naphthalene represent two ring hydrocarbons etc. The composition, properties and quantity of tar in producer gas vary remarkably depending upon the biomass feedstock, gasifier type and gasification conditions [1].

Typical tar compounds derived from biomass gasification can be classified into primary, secondary and tertiary tar categories, as shown in Fig.1. The primary tar compounds are produced during pyrolysis process. It reacts with surrounding species and converts into secondary tar at relatively higher temperature and subsequently into tertiary tar compounds. Tertiary tar compounds are very stable which mainly consist of Poly-aromatic hydrocarbons (PAH), benzene, naphthalene etc. It is available in ample amount during biomass gasification process.

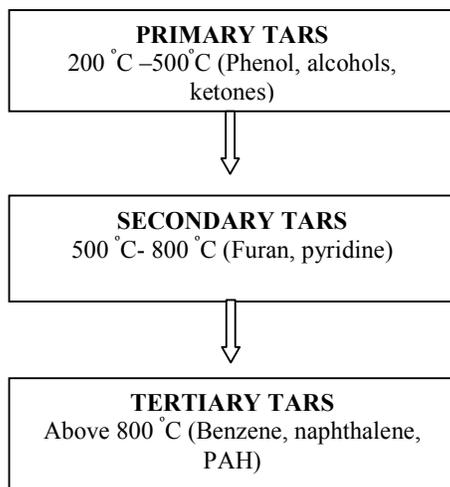


Figure 1: Classification of tar

Cleaning of syngas produced in biomass gasification process is necessary when biomass used as a fuel in power producing system like gas turbine, inter-combustion engines etc. Two basic approaches have been used to remove tars from producer gas [9], [10].

- Physical tar removal methods.
- Catalytic and thermal cracking of tar.

Physical Tar Removal Methods

Tars are generally removed from the producer gas by cooling the product gas, leading to condensation of tar into aerosol droplets and then removing the droplets by using different processes. These processes are mainly wet scrubbers, electrostatic precipitators etc. [10] -[12].

In wet scrubber technology, tars are collected through the impingement of the product on water drops. Flow of tar and liquid takes place through demister and tar are removed from the aqueous plane. There are many designs of scrubber such as spray towers, impingement scrubbers and baffle scrubbers. Cooling towers are the first wet scrubbing units where the heavy tars condense. But tar droplets and gas/liquid mists are removed by the gas flow which makes this process inefficient.

Electrostatic precipitators (ESP) are widely used to remove tars from gas streams. These are effective with liquid droplets but are not suitable when tar is in gaseous state. This means that this process is inefficient when the tar is in gaseous state. Here, the gas streams are passed through a high voltage, negatively charged area leading to the charging of particles. The opposite charged plate is used to remove these charged particles from the streams. The conductivity of ESP is very much dependent on the nature of tar. Hence, the characteristics of tar plays a major role in designing of the ESP. Tar can be removed from biomass gasifier gas only by wet ESP because condensation on dry ESP precipitation electrode would hinder the particle removal.

Catalytic and Thermal Cracking of Tar

Thermal and catalytic cracking processes are used to convert high molecular mass tar component into lower molecular mass components and useful gas components. Not only catalytic and thermal cracking processes reduce tars, but also enhance the heating value by increasing the amount of H_2 in the product gas [3], [13]. These processes are very effective as they lead to increase conversion efficiency.

Thermal cracking is the oldest process of tar cracking. In this process the temperature is increased to an extent such that the heavy tar compounds cracks into smaller ones such as, carbon monoxide, methane and hydrogen. In above process some amount of hydrogen or air is supplied as per requirement. For this process temperatures should be kept above 900 °C so that tar reduces significantly. Steam has also been used as an input parameter to crack the tar into lighter component and useful gas species.

Catalytic cracking is one of the most promising techniques for tar cracking in which the tar compounds are reformed into useful gas species in the presence of suitable catalysts. The catalytic cracking of tar can be done in two ways. Either catalyst is used with the biomass in the biomass gasifier or tar

compounds are passed over a catalyst bed. Selection of catalyst is one of the most important factors in the catalytic conversion. The amount of gas species in the producer gas and the temperature of conversion are highly dependent on catalysts. Many chemical reactions take place simultaneously during thermal cracking which is shown in Fig. 2.

There are two kinds of catalysts used: metallic and non-metallic oxide. The first one is metallic oxide such as Ni based catalyst [8], Al_2O_3 ,

SiO_2 , MgO , $\text{MgO}-\text{Al}_2\text{O}_3$, $\text{SiO}_2-\text{Al}_2\text{O}_3$ [14]. Second one is non-oxide such as calcined dolomites, char [15], olivine and zeolites. It is seen that the conversion of tar from the process with the catalyst are in the range of 57 to 86%. This is higher than the reaction without catalyst which has conversion efficiency of 26 to 34%. Main products forms in this process are CO , H_2 and smaller molecular mass hydrocarbon like C_3H_6 , CH_4 , C_2H_6 . Catalytic reforming of tar is done at lower temperature than thermal cracking.

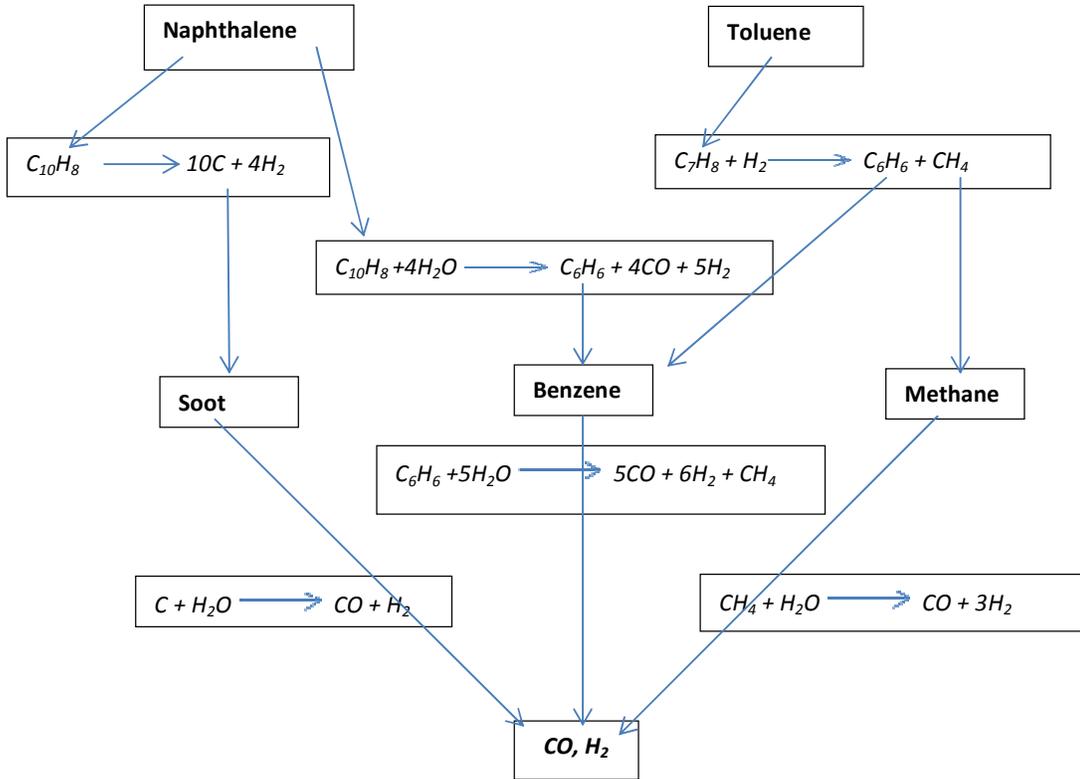


Figure 2: Reaction Taking Place During Thermal Cracking TAR

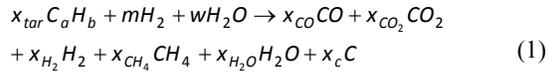
TAR CRACKING MODEL

The composition of producer gas or syngas has been estimated during thermal cracking of tar by supplying steam and hydrogen. Mass balance equation and equilibrium constant have been used to evaluate the gas composition. Gibbs free energy minimization principle and three auxiliary equations viz. water-gas shifting (WGS) reaction, methane cracking reaction, methane steam reforming reaction have been used for calculation of equilibrium gas constants. Three tar compounds namely benzene, naphthalene and toluene are considered which contributes major portion of total tar produced during biomass gasification. An equilibrium tar model of these three compounds have been developed and analyzed in the following section. Several assumptions have been adopted for carrying

out the analysis. The main assumptions considered are as follows:

- Reactor's temperature is assumed to be constant.
- Reactor operates at pressure = 101.325 kPa.
- Steady state operation has been considered.
- Gases obey ideal gas principles.
- Heat losses from the components are neglected.
- Equilibrium condition is assumed for all the reactions.

The chemical formula of the tar is assumed as C_aH_b and corresponding reaction for thermal cracking of tar in the presence of hydrogen and steam can be stated as,



where a is the number of carbon atom in the tar and b is the number of hydrogen atom in the tar (benzene, toluene, naphthalene); x_{tar} is the number of moles of tar; m is the number of moles of hydrogen and w is the number of moles of steam; and x_{CO} , x_{CO_2} , x_{H_2} , x_{CH_4} , x_{H_2O} , x_C are the number of moles of CO, CO₂, H₂, CH₄, H₂O, C(soot) respectively produced in the reaction.

The mass balance equations for carbon, hydrogen and oxygen are as follows respectfully

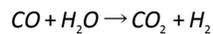
$$x_{CO} + x_{CO_2} + x_{CH_4} + x_C - a \times x_{tar} = 0 \quad (2)$$

$$2 \times x_{H_2} + 4 \times x_{CH_4} + 2 \times x_{H_2O} - b \times x_{tar} - 2 \times m - 2 \times w = 0 \quad (3)$$

$$x_{CO} + 2 \times x_{CO_2} + x_{H_2O} - w = 0 \quad (4)$$

Many chemical reactions occur during tar cracking process. The most probable three equations are needed to be assumed. WGS reaction, methane steam reforming and methane cracking reaction have been taken into consideration for the present analysis.

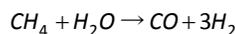
The first reaction is water gas shift reaction in which CO gas reacts with steam and produced CO₂ and H₂ as shown below.



For this reaction, the equilibrium constant (K_1) in terms of number of moles of reactant and product side and in term of Gibbs free energy are:

$$K_1 = \frac{x_{CO_2} \cdot x_{H_2}}{x_{CO} \cdot x_{H_2O}} = \exp \left(- \left(G_{CO_2}^{\circ} + G_{H_2}^{\circ} - G_{CO}^{\circ} - G_{H_2O}^{\circ} \right) / RT \right) \quad (5)$$

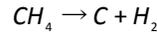
The second reaction represents methane steam reforming reaction in which methane react with steam and produced CO and H₂.



And its equilibrium constant (K_2) is written below.

$$K_2 = \frac{x_{CO} \cdot (x_{H_2})^3}{x_{CH_4} \cdot x_{H_2O}} = \exp \left(- \left(G_C^{\circ} + 2 G_{H_2}^{\circ} - G_{CH_4}^{\circ} \right) / RT \right) \quad (6)$$

The third reaction is methane cracking reaction in which methane breaks into C (soot) and H₂ as shown below.



And corresponding equilibrium constant K_3 is given below.

$$K_3 = \frac{x_C \cdot (x_{H_2})^2}{x_{CH_4}} = \exp \left(- \left(G_C^{\circ} + 2 G_{H_2}^{\circ} - G_{CH_4}^{\circ} \right) / RT \right) \quad (7)$$

where G° stands for standard Gibbs free energy. It is defined as below.

$$G_T^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \quad (8)$$

These equations (Eqn.2-8) have been solved by Engineering Equation Solver (EES) software. The solution of these equations estimated the composition of product gases at different temperature and different steam to carbon (S/C) ratio.

RESULTS AND DISCUSSION

Input parameters used for the analysis are shown in Table 1.

Table 1: Parametric assumption

Input parameter	Value
Number of moles of tar(x_{tar})	1
Number of moles of steam(w)	10
Number of moles of H ₂ (m)	4
Temperature	1073-1523 K
Steam to carbon ratio	1-6

Cracking of Benzene as a Tar Model

The effect on outlet gas composition when temperature is varied from 1073–1523K, during the thermal cracking of benzene (C₆H₆) in presence of hydrogen & steam is shown in Fig.3. It is seen from Fig.3 that as the temperature increases, percentage of CO and H₂ increases while percentage of CO₂, CH₄ and C (carbon soot) decreases.

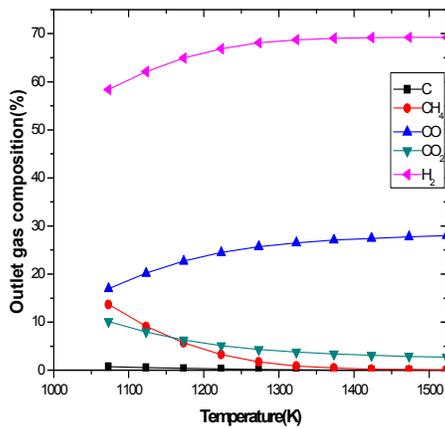


Figure 3: Temperature variation on the outlet gas composition of benzene at S/C=3

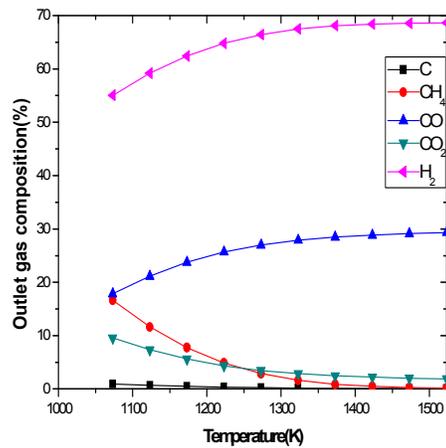


Figure 5: Temperature variation on the outlet gas composition of toluene at S/C=2.143

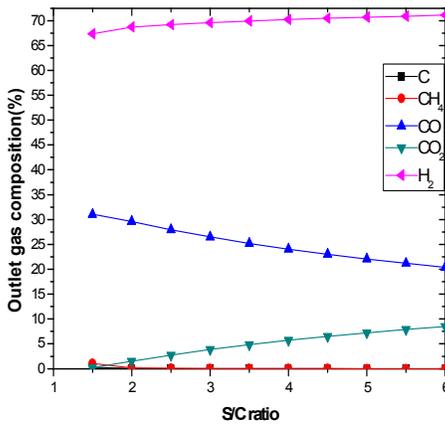


Figure 4: S/C ratio variation on the outlet gas composition of benzene at T=1513 K

Fig.4 shows that the composition of outlet gas after thermal cracking of benzene with rising the S/C ratio. It is found from Fig.4 that as the steam to carbon ratio increases, the percentage of H₂ and CO₂ increases whereas percentage of CO and CH₄ decreases. It is also found that the amount of carbon (soot) formation during the thermal cracking of benzene is negligible.

Cracking of Toluene as a Tar Model

Fig.5 depicts the variation in product gas composition with changing reaction temperature after the thermal cracking of the toluene. It is seen from Fig.5 that as the temperature increases, the percentage of CO and hydrogen

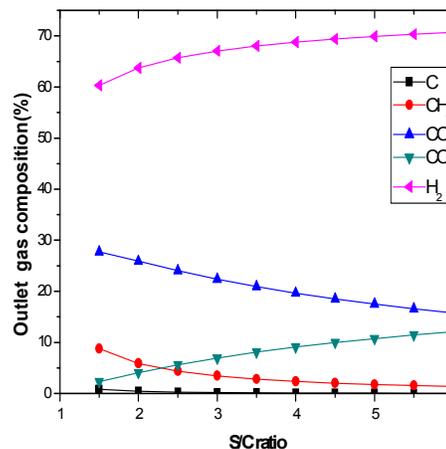


Figure 6: S/C ratio variation on the outlet gas composition of toluene at T=1213 K

increases while the percentage of C, CO₂ and CH₄ decreases. Fig.6 depicts the variation of product gas composition for toluene with changing S/C ratio at fixed temperature and hydrogen supply. Steam is consumed in methane reforming reaction. Hence, the amount of methane decreases with increasing S/C ratio. It is shown in Fig.6 that as the S/C ratio increases, the percentage of CO₂ and H₂ also increases while the percentage of CO decreases. It is because steam enhances the WGS reaction rate which attributed to increase of CO₂ percentage.

Cracking of naphthalene as a tar model

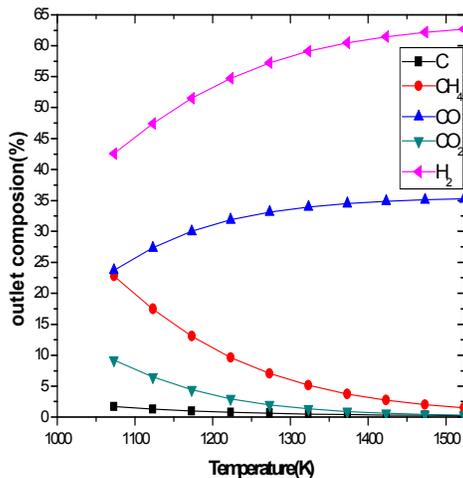


Figure 7: Temperature variation on the outlet gas composition of naphthalene at S/C=1.5

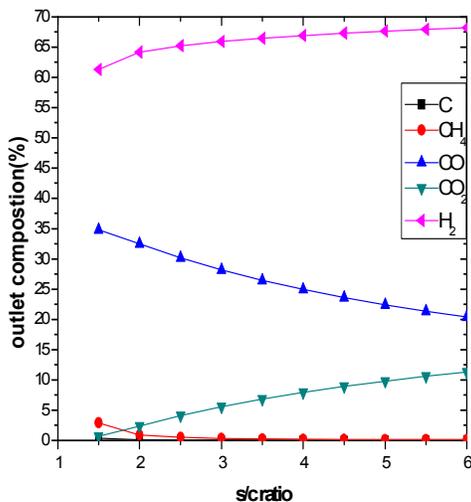


Figure 8: S/C ratio variation on the outlet gas composition of naphthalene at T=1423 K

Fig.7 shows the variation of outlet gas composition of the thermal cracking of naphthalene with temperature. It is seen from Fig.7 that the percentage of CO and H₂ increases with increase in temperature while percentage of CH₄ and CO₂ decreases. It is also found that at lower temperature, the percentages of CH₄ and soot formation are higher for naphthalene as compared to other tar compounds.

Fig.8 shows the variation of outlet gas compositions of the thermal cracking of naphthalene with the effect of steam to carbon ratio at constant H₂

supply. Hydrogen yield is significantly high as shown in Fig.8. Percentage of CO₂ increases but percentage of CH₄ decreases with increase in S/C ratio.

CONCLUSION

In this paper, major techniques and processes for tar removal have been discussed. An equilibrium tar cracking model has been developed and analyzed for three tar compounds namely toluene, benzene and naphthalene. The effects of major operating parameters such as temperature and S/C ratio on the product gas constituents have been reported. Major conclusions are follows:

- The percentage of H₂ and CO increases with increasing reaction temperature whereas the percentage of C, CO₂, and CH₄ decreases for all tar compounds.
- The percentage of H₂ and CO increases with increasing S/C ratio whereas the percentage of C, CO, and CH₄ reduces for all tar compounds.
- Substantial amount of soot (C) has been formed at lower S/C ratio during the thermal cracking of naphthalene compared to other tar compounds.
- Amount of H₂ gas in product gas is almost constant beyond a fixed temperature depending on the type of the tar.

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