Kinetic Modeling of Tar Formation in an Updraft Biomass Gasifier

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ABSTRACT

As the depreciation of the fossil fuels in the world, it is obligatory to discover new fuels to the highly industrialized society. With increasing requirements of the energy, it is globally focused on the use of renewable energy. Biomass can be used as an alternative energy source to replace fossil fuels, which contribute to the greenhouse gas emission. Therefore, biomass is a major renewable energy source as of today.

Nowadays, converting biomass into biofuel is a major goal. So, the gasification process can be used as such an effective way to convert biomass into syngas. Even if the major goal of the gasification is to produce syngas such as H_2, CO, intermittently, many byproducts are generated such as NO_x, SO_2, fly ash and tar. The formation of tar in the gasifier is a problematic situation. The formation of tar mainly depends on temperature, residence time, type of biomass and gasifying medium.

Modeling is an effective method to optimize the gasifier operation. Also, it can be used to determine the relationship between operational parameter limits and explain trends in output products. By using Aspen Plus process simulation tool, a kinetic model was developed to predict the tar formation of updraft gasifier considering the main chemical phenomena biomass pyrolysis, reduction and combustion. The results were compared with the experimental data from the literature to validate the model. According to the developed model, the tar content and the composition could be estimated with respect to the equivalence ratio (ER) and pyrolysis zone bed height. When the ER is increasing the formation of tar is trending to decrease. The pyrolysis zone bed height beyond 1.3 cm does not show a significant impact on the tar content.

It is possible to use the developed model to minimize tar content by operating at a suitable temperature (by controlling the ER) and by keeping an applicable residence time (by maintaining a suitable bed height). Further, this model can be used to optimize the tar formation with different biomass types and gasifying mediums when the temperature profile of the gasifier is available.

Keywords: Biomass, Updraft Gasifier, Tar, Kinetic Modeling

NOMENCLATURE

Abbreviation	**Description**
ER	Equivalence Ratio
PFR	Plug Flow Reactor

Symbol	**Description**
$C_7H_8O_2$	Guaiacol
$C_8H_8O_3$	Vanillin
C_6H_6O	Phenol
$C_7H_6O_2$	Salicylaldehyde
$C_6H_6O_2$	Catechol
C_7H_8O	o-Cresol
$C_{10}H_8$	Naphthalene
$C_{14}H_{10}$	Phenanthrene
C_6H_6	Benzene
C_5H_6	Cyclopentadiene
C_9H_8	Indene
C	Concentration (mol/m^3)
k	Reaction rate constant (1/s)
r	Reaction rate (mol/m^3s)
R	Universal gas constant (J/mol K)
T	Temperature (K)

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Chapter 1

1.1 Introduction

Biomass is an environmentally friendly renewable energy source. Therefore, nowadays converting biomass into biofuel is a trend of producing bioenergy. Thermochemical process and biochemical process are the available methods used to convert biomass into bioenergy[1]. Combustion, gasification and pyrolysis are the main methods used to produce bioenergy from biomass through thermochemical conversation [2]. Among them pyrolysis is mostly affected to the product yield and composition.[3]

Biomass gasification is one of the most important techniques to produce syngas. Syngas is used as a chemical feedstock or syngas is directly utilized as a fuel to generate heat, electricity or both [4]. As a result of the gasification, mainly gases, solids and condensable tars are formed from carbonaceous materials. H_2, CO and CH_4 are the main gaseous products of the gasification. Except those gases there are undesired products such as N_2 and CO_2 and considerable amount of tar compounds. The overall reaction related to the gasification process is shown in Equation 1 [1]

$$\begin{aligned} Biomass + O_2\,(or\ H_2O) \quad &\rightarrow CO, CO_2, H_2O, CH_4 + other\ hydrocarbons \\ &\rightarrow Tar + Char + Ash \\ &\rightarrow HCN + NH_3 + HCl + H_2S + other\ sulfur\ gases \end{aligned}$$

Equation 1: Reaction related to gasification

During gasification, in addition to syngas, formation of tar is unavoidable. As tar condense on cold surfaces and polymerize in pipes and filters it results in blockage [5]. Further, the tar content in the syngas limits its direct use in engine applications [2]. Therefore, to limit the tar formation, it is essential to find an additional removal technique [2]. Optimizing gasification conditions while the gasification process is undergoing (Primary method) or using post-gasification treatments (Secondary method), can be used to overcome the problem of tar [6].

Chapter 2: Literature review

2.1 Gasifier types

According to the bed type used in the gasification process, there are three main types of gasifiers called fixed bed, fluidized bed and entrained flow gasifiers [7].

2.1.1 Fixed bed gasifier

When the gasifier bed is filled with solid fuel particles, this gasifier is called as fixed bed gasifier. The media to proceed the gasification can be air, steam, oxygen or a mixture of them [4]. Compared to other gasifiers, the fixed bed gasifier is more cost effective for small scale applications. But, due to poor heat transfer and inhomogeneous temperature the process is slow.

2.1.1.1 Updraft gasifier

In updraft gasifier biomass feed moves downward and the gasifying agent moves upward counter-current to biomass through the fixed bed of biomass. This type has a higher thermal efficiency due to the combustion takes place at the gasifier bed bottom, then, hot gases pass through reduction, pyrolysis and drying zones of the bed providing necessary heat (see Fig. 1). As a result, the final product syngas exits from the top of the gasifier at relatively lower temperature. In an updraft gasifier, comparatively high moisture fuels can be used since thermal energy to dry the biomass can be supplied from gases coming from the pyrolysis zone[8]

2.1.1.2 Downdraft gasifier

The process in downdraft gasifier is also similar to updraft gasifier. But gasification agent flows co-current to the fuel (see Fig. 1). Because of the product gas exits from the bottom of the gasifier tar levels in the product gas get lower than updraft gasifier.

2.1.1.3 *Cross draft gasifier*

In a cross-draft gasifier, the gasifying media and gas are flowing horizontally through the reactor [4]. Also the ash bin, combustion and reduction zones are separated from each other (see Fig. 1). Because of the higher operating temperature, the product gas also has a higher temperature.

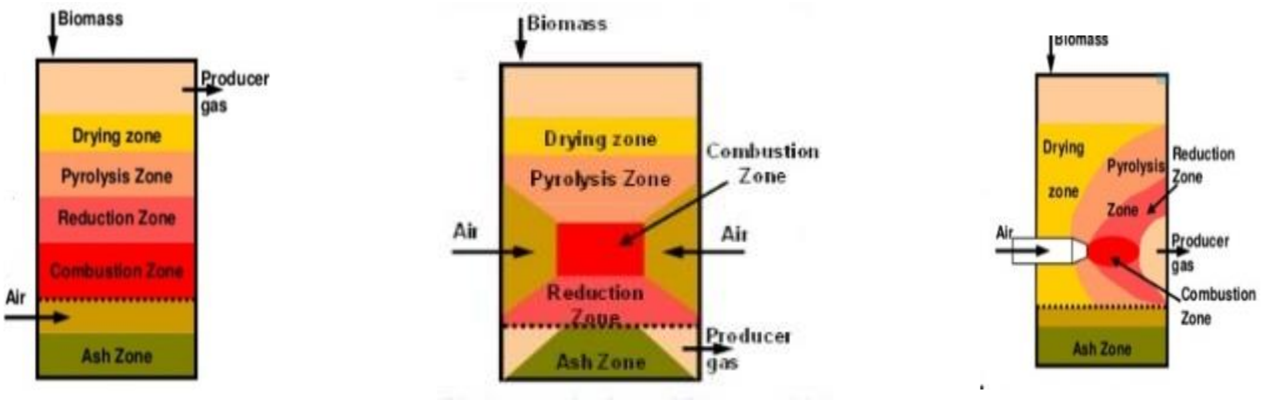


Figure 1. From left to right, Updraft gasifier, Downdraft gasifier, Cross draft gasifier

2.1.2 Fluidized bed gasifiers

In fluidized bed gasifier it is essential to use a bed medium. The bed medium is silica or alumina. In a fluidized bed gasifier biomass is input from the bottom of the gasifier and ash is removing as dry ash (see Fig. 2). Fluidized bed gasifier is designed as a cylindrical column [4]. By applying a bed medium and having good mixing inside the gasifier, it results in enhanced heat and mass transfer increasing the reaction rates and conversion efficiencies [7].

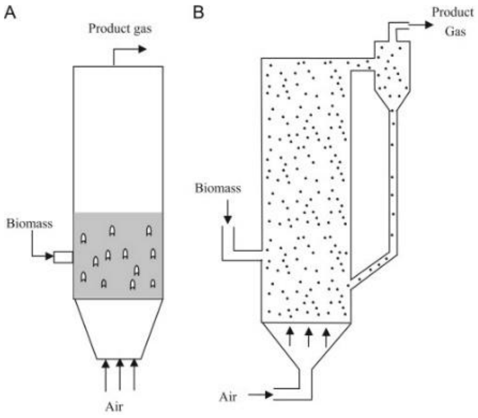


Figure 2: Fluidized bed gasifier

2.1.3 Entrained flow gasifiers

A vertical and cylindrical vessel is used as an entrained flow gasifier (see Fig. 3). Under this gasification process, oxygen is commonly used as an oxidant to operate the process. As a byproduct ash slag is formed. An entrained flow gasifier can operate at higher temperatures than other gasifiers. The advantage of this gasifier is the high temperature, which limits the formation of tar and methane in the producer gas.

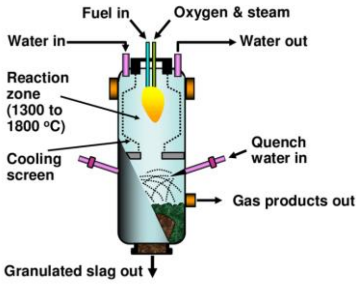


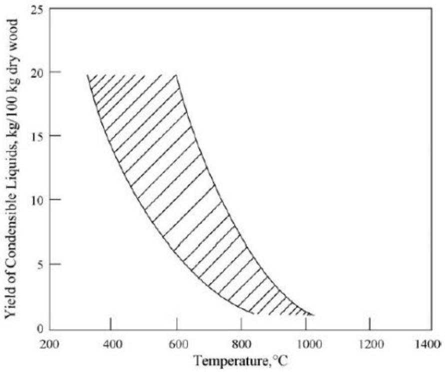
Figure 3: Entrained flow gasifiers

2.2 Biomass tar

In a gasifier, even if the aim is to completely convert carbon, normally a certain amount of carbon is present in the ash and tar [1]. For the process of gasification, tar formation is essential for the stabilization [9]. But, formation of tar while gasification acts as a major problem. It results in fouling in the gas cooler or gas cleaning equipment. Because of this, the maintenance cost can be getting higher. Therefore, there should be an ultimate goal to eliminate the formation of tar during gasification [10].

When considering biomass, the main components of biomass are cellulose, hemicellulose and lignin [1]. Among those three main components, lignin is the major factor for the formation of biomass tar. In the gasification process formation of tar is occurring as a resulting of a complex reaction series [9]. Therefore, tar is a mixture of condensable hydrocarbons (and oxygen), from single ring up to five ring aromatic compounds [10]. Because of that, the formation of tar highly depends on the reaction conditions in the gasifier such as temperature, equivalence ratio (ER), type of the biomass, pressure, gasifying medium and residence time (see Fig. 4)[1],[5].

Tar is derived from polycyclic aromatic hydrocarbons (PAH) including Benzene, which are assembled while processing the thermochemical reaction series. Therefore, so many research articles express the formula of the tar as $C_6H_{6.6}O_{0.2}$. For occurring these reactions, thermochemical kinetics are highly involved [11]. When the definition of the biomass tar is simplified, it can be defined tar as the higher molecular weighted hydrocarbons which are difficult to remove by thermochemical process [1].



"Tar" yield as a function of the maximum temperature exposure

Figure 4: Tar yield vs temperature

2.3 Tar classification

According to the molecular weight of the tar compounds, it can be seen on some research articles divided tar components, mainly into three classes as primary tars, secondary tars and tertiary tars [1].

Primary tars **-** *The source of the primary tars is cellulose, hemicellulose and lignin. Due to decomposition of cellulose, hemicellulose and lignin primary tars are emerged from the pyrolysis process in the gasifier* [9].

Secondary tars **-** *According to the increase of temperature in the gasifier, primary tars tend to form secondary tars reacting with mostly substituted phenol, occur from lignin* [9].

Tertiary tars - *Tertiary tars can be found at temperature above 800* ^{O}C*, emerge from small molecule fragments which form additional cyclohexane rings imitated by an aromatization because of the dehydrogenation and dehydration respectively* [9].

The transition of tars depending on the temperature is depicted in Equation 2 [9].

$$\frac{\begin{array}{c}Mixed\\ Oxygenates\end{array}}{400℃} \rightarrow \frac{\begin{array}{c}Pheycolic\\ Eathers\end{array}}{500℃} \rightarrow \frac{\begin{array}{c}Alkyl\\ Phenolics\end{array}}{600℃} \rightarrow \frac{\begin{array}{c}Heterocylic\\ Eathers\end{array}}{700℃} \rightarrow \frac{PAH}{800℃} \rightarrow \frac{\begin{array}{c}Larger\\ PAH\end{array}}{900℃}$$

Equation 2: Temperature of transition of tars

According to molecular weight, there is another tar classification as listed in Table 1.

Table 1: Classification of tars based on molecular weight

Tar Class	**Class name**	**Representative compounds**
1	GC-Undetectable	Very heavy tars
2	Heterocyclic aromatics	Pyridine; Phenol; Cresols; Quinoline; Isoquinoline; Dibenzophenol
3	Light aromatic (1 ring)	Toluene; Ethyl benzene; Xylenes; Styrene
4	Light PAH compounds (2-3 rings)	Indene; Naphthalene; Methylnaphthalene; Biphenyl; Ace naphthalene; Fluorene; Phenanthrene
5	HeavyPAHcompounds (4–7 rings)	Fluoranthene, pyrene, chrysene, perylene, coronene

2.4 Tar destruction

Cracking, steam and dry reforming, carbon formation and partial oxidation reactions cause the decomposition of tar. They are multiple and simultaneous reactions [5]. In the below reactions(Equation 3) C_nH_x represents tar and C_mH_y represents hydrocarbons with smaller carbon number than C_nH_x.

Thermal cracking

$$pC_nH_x \leftrightarrow qC_mH_y + rH_2$$

Steam reforming

$$C_nH_x + mH_2O \leftrightarrow nCO + \left(m + \frac{x}{2}\right)H_2$$

Dry reforming

$$C_nH_x + nCO_2 \leftrightarrow 2nCO + \left(\frac{x}{2}\right)H_2$$

Carbon formation

$$C_nH_x \leftrightarrow nC + \left(\frac{x}{2}\right)H_2$$

Partial oxidation

$$C_nH_x + (\frac{n}{2})O_2 \leftrightarrow nCO + \left(\frac{x}{2}\right)H_2$$

Equation 3:Set of reactions for tar destruction

2.5 Methods of tar modelling

According to the previous research publications, there are some studies available on modeling of tar. Existing methods for the modeling of tar can be divided into three main categories [5].

1. Single compound models
2. Lumped models
3. Detailed kinetic models

2.5.1 Single compound models

From the experimental data, which is done for identification of tar compounds and compositions, single component has been selected. For this, the most abundant individual tar species are considered as tar model compounds including Naphthalene, Toluene, Cresols, Phenols and some primary tars like Guaiacols.

Naphthalene has been studied under pyrolysis conditions in a mixture of hydrogen and steam environment. After cracking Naphthalene under pyrolysis conditions Benzene, Methane, C_2 Hydrocarbons were produced as the main products and Indene, Dihydro-naphthalene and Toluene were produced as minor products. Also Soot was produced. By cracking soot and hydrocarbons CO and CO_2 were originated.

Toluene is a hardly destructible aromatic compound produced while pyrolysis. Therefore, Toluene has also been chosen as a tar model. From this, a thermodynamic model was developed for the pyrolysis of biomass, as well as constraints on carbon have been placed to allow Toluene to produce other thermodynamically unstable hydrocarbons such as Benzene, Styrene, Phenol and Naphthalene.

When considering Phenol as a tar model, Phenol is cracked into Naphthalene and Benzene. And also, due to undergoing decomposition of Phenol, Benzene and Naphthalene, water and non-condensable gases are formed as the products [5].

2.5.2 Lumped models

Under this model it has been assumed that all the tar compounds are formed as a single lump.

For Miscanthus and wood pallets gasification, there is an assumption that tar undergoes a single decomposition step during flash pyrolysis, according to the Equation 4 where $C_xH_yO_z$ represents tar [5]. Also, there is an assumption that all the tar species react according to the first order kinetic model. The kinetic parameters are derived from TG-FTIR analysis of the flash pyrolysis step including tar production. [12]

$$C_xH_yO_z \rightarrow zCO + \frac{1}{4}CH_4 + \left(x - y - \frac{1}{4}y\right)C$$

Equation 4: Reaction occurring in lumped model

An advanced kinetic model has been developed to treat tar as six lumps [13]. They are Benzene, other one ring compounds, Naphthalene, other two ring compounds, three and four ring compounds, Phenolic compounds. By considering experimental work on the evolution of tar composition, the mechanism is considered as a set of six kinetic equations with eleven kinetic constants. The main features identified from this model are Phenolic compounds are more reactive and Naphthalene is the most stable compound to be destroyed. Kinetic equations are fitted with the experimental data. Heavy tar compounds have been neglected due to those might condense even at higher temperatures and lower concentrations.[5]

2.5.3 Detailed kinetic models

This model category was developed, which involve reaction mechanisms comprising hundreds of elementary steps like reactions, in order to provide a more accurate description of the gas phase reactions concerning aromatic growth [14].

To predict the mechanism of de-volatilization of lignin from TGA pyrolysis experiments, a "semi detailed" kinetic mechanism has been proposed [15]. For this model, 3 reference lignin units have used to represent the initial lignin structure. 100 molecular and radical species have considered as intermediates. Experimental TGA literature data from a variety of pyrolysis lignin have compared with the model prediction and the results agreed with the experimental thermal degradation of lignin.

To predict the steam reforming of aromatic hydrocarbons, a reaction mechanism comprising 257 chemical species from Hydrogen radicals to Coronene, and 2216 reactions have been used [16]. Comparison of the experimental data from thermal conversion of Naphthalene, Benzene and Toluene with the model had good agreement.

A detailed kinetic model has been applied to gas phase reactions involved in the secondary pyrolysis of cellulose [17]. For this model, elementary reactions have used from an automatic reaction generating software. Because of this model has used more than 500 species and more than 8000 reactions, the model is more complicated to evaluate.

2.6 Aspen Plus tar models

Aspen Plus is a modeling software used for designing a new process, troubleshooting a process unit or optimizing operations [18] by using suitable unit operations such as reactors, separators, heat exchanges. And also the models can be designed according to the physical properties of the materials [19].

A comprehensive mathematical model has been designed for a combined heat and power (CHP) incorporating a biomass bubbling fluidized bed gasification unit by using Aspen Plus, considering the kinetic and equilibrium parameters. In this model, the total tar content has been assumed to be 20% of biomass. A mixture of Benzene, Toluene and Naphthalene have been considered as the tar components produced in the pyrolysis zone and the formation of these components have been fixed in the model with 60%, 20% and 20% for Benzene, Toluene and Naphthalene, respectively. Decomposition of these three reference tar components to CO_2, H_2

and CO has been modeled using their oxidation reaction kinetics. The model has been simulated with changing temperature and changing ER. The results have been validated with experimental data [20]

An Aspen Plus model has been designed by a combination of a solid oxide fuel cell (SOFC) with biomass steam gasification process and Combined heat and power (CHP) system. Here, referring to the relevant literature, a fixed tar amount has been set in order of 1–5 g/m^3 in dry basis produced gas using stoichiometric reactor block to represent the tar formation[21].

By combining a biomass gasification fuel cell (BGFC) and biomass gasification combined cycle (BGCC) systems, an Aspen Plus model has been designed to compare the energetic and emission performance of both systems. This was done considering Phenol as the tar model compound[22]

Aspen Plus has also been used to model a Biomass Integrated Gasification Combined Cycle (BIGCC) to estimate the renewable energy of ethanol production. In this study also, tar has been modeled as Phenol.[23]

For a dual fluidized bed gasifier integrated with combined heat and power (CHP) plant, an Aspen Plus model has been designed considering a mixture of Benzene, Phenol, Toluene and Naphthalene as the tar components produced in the pyrolysis zone. Here, the tar cracking reactions have been kinetically modeled in a plug flow reactor and adjusted with experimental data [24]

An Aspen plus model has been developed for pressurized steam/O_2-blown Fluidized-Bed gasification for biomass to calculate the tar conversion. In this model, tar has been modeled as Naphthalene and tar conversion correlations have been used from the experimental data [25]

To predict the performance of gasification of Dried Sewage Sludge (DSS), a staged-gasification system has been developed by using Aspen Plus. In this model, there are three main stages such as de-volatilization of the fuel, homogeneous gas reforming/oxidation of volatiles and heterogeneous reforming reactions of gas over in situ generated char. Tar has been modeled as Toluene and oxidation of tar has been kinetically modeled in a plug flow reactor [26].

2.7 Influence of equivalence ratio

When considering biomass gasification, equivalence ratio (ER) is one of the most important factors to be considered. The ER is the ratio of the actual air-fuel ratio to the stoichiometric air-fuel ratio. For an updraft gasifier, the typical ER value varies between 0.1 and 0.3 [27]. When more oxygen is supplied into the gasifier, the combustion reactions tend to undergo more efficiently as well as at a higher temperature [27]. Therefore, ER value is a kinetic factor that affects the chemical reaction. That’s why the reaction rate highly depends on the ER value. In biomass gasification the ER value affects the composition of the syngas as well as the composition of the tar. The gasifier size, chemical and physical properties of the biomass used are also having an effect on the ER value.

Chapter 3: Research objectives

There are many studies on tar formation of downdraft gasifiers [21] and fluidized bed gasifiers [21]. For updraft gasification, only experimentation has been carried out on the formation of tar and composition of tar. Since syngas obtained from updraft gasifiers contains considerably higher tar content compared to downdraft and fluidized bed gasifiers, studying tar formation in updraft gasifiers is equally important. Therefore, this study is aimed at understanding the tar formation in updraft gasifiers so that tar formation is minimized by controlling the operating conditions or design parameters. In order to achieve this anticipated aim following research objectives are set;

1. Study the effect of the equivalent ratio (ER) on the gas composition, tar content and tar composition of the syngas produced.
2. Study the variation of tar content and tar composition along the gasifier bed height.

Chapter 4: Materials and Methodology

4.1 Fuel

Beech wood was taken as the fuel type for gasification. This is the same fuel type that used in the experimental study of characteristics of tar content and syngas composition which was used as the basis for this modeling study [7]. Proximate and ultimate analysis of cellulose, hemicellulose and lignin in the beech wood are presented in Table 2 and Table 3.[8]

Table 2: Ultimate analysis

Property	Carbon (%)	Hydrogen (%)	Oxygen (%)
Cellulose	42	6.24	51.76
Hemicellulose	40.14	6.65	53.21
Lignin	61.68	5.85	32.47

Table 3:Proxymate analysis

Property	Moisture (%)	Volatiles (%)	Fixed Carbon (%)
Cellulose	5.20	83.05	11.93
Hemicellulose	0.01	98.33	1.66
Lignin	2.99	60.60	36.41

4.2 Aspen Plus model

A model for updraft gasifier was simulated using Aspen Plus V10.0. The gasifier was modeled by using, combustion zone, reduction zone and pyrolysis zone. The model was developed by assuming only the lignin fraction of wood is responsible for the majority of tar formation during primary pyrolysis. According to the detailed kinetic model for lignin devolatilization, about hundreds of elementary step like reactions are occurring and as the products of devolatilization as much as hundreds of species are formed which results in a complex problem while simulating [1],[11]. Therefore, pyrolysis was started with three reference lignin units $C_6H_6O_2$, $C_7H_8O_2$ and $C_8H_8O_3$ which are the main constituents of lignin.

A combination of a Yield reactors and a Gibbs reactor were used to model the reduction and combustion zones in equilibrium. First, cellulose, hemicellulose and lignin were defined as non-conventional solids with defined proximate and ultimate analysis. They were fed by using three Yield reactors (CELYIELD/HEMYIELD/LIGYIELD) separately as per the biomass composition. To perform the reactions with Gibbs energy minimization, the output streams were sent to the Gibbs reactor (GIBBS). For lignin, only the fixed carbon fraction was separated using a Separator (FCSEP) and sent to the Gibbs reactor. Air flow rate was adjusted considering the operating equivalence ratio (ER). A Plug Flow Reactor (PFR) was used to represent the tar formation, cracking and reforming in the pyrolysis zone. The output stream of the Gibbs reactor and volatile fraction of lignin were sent to the Plug Flow Reactor (PFR) through a Mixer (MIX) (see Fig. 5).

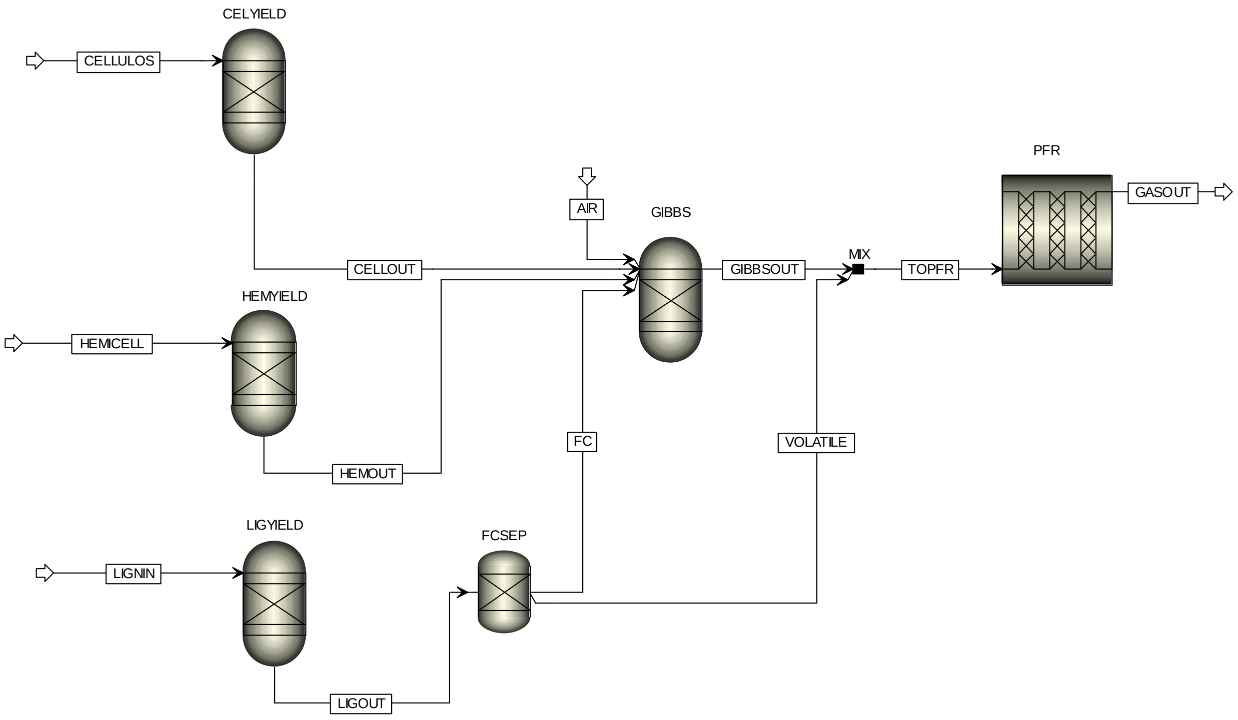


Figure 5: Aspen Plus model for the updraft gasifier

Following homogeneous gas phase reactions(Equation 5) were considered as the tar formation, cracking and reforming reactions happening in the pyrolysis zone [10] and were added to the PFR model.

(R1) $C_8H_80_3 \rightarrow C_7H_8O_2 + CO$

(R2) $705C_7H_80_2 \rightarrow 470C_6H_60_2 + 40C_6H_6O + 70C_7H_8O + 150C_7H_6O_2 + 275CH_4 + 60CO + 10H_2$

(R3) $C_6H_6O_2 + 2H_2 \rightarrow C_6H_6 + 2H_2O$

(R4) $C_6H_6O_2 \rightarrow C_{10}H_8 + 2CO_2 + 2H_2$

(R5) $C_6H_6O \rightarrow C_5H_6 + CO$

(R6) $3C_6H_6O_2 \rightarrow C_{14}H_{10} + 4CO + 2H_2O + 2H_2$

(**R7**) $2C_5H_6 \rightarrow C_{10}H_8 + 2H_2$

(**R8**) $C_{10}H_8 + O_2 \rightarrow C_9H_8 + CO_2$

(**R9**) $C_8H_8O_3 + 6.68H_2 \rightarrow 2.66CO + 0.085CO_2 + 5.255CH_4 + 0.17H_2O$

(**R10**) $C_9H_8 + C_5H_6 \rightarrow C_{14}H_{10} + 2H_2$

(**R11**) $C_{10}H_8 + 4H_2O \rightarrow C_6H_6 + 4CO + 5H_2$

(**R12**) $C_6H_6 + 3O_2 \rightarrow 6CO + 3H_2$

Equation 5: Set of reactions added to the PFR reactor

Table 4 represents the kinetic data [10] added to the PFR model.

Table 4: Kinetic parameters of reactions involved in the kinetic model

Reaction Number	**Reaction Rate (mol/m^{3}s)**	**Kinetic coefficient (concentration is mol/m^3)**
R1	$r_1 = k_1 C_{C_8H_8O_3}$	$k_1 = 1.3\text{x}10^{11}\exp(-175309/RT)$
R2	$r_2 = k_2 C_{C_7H_8O_2}$	$k_2 = 1.58\text{x}10^{12}\exp(-191000/RT)$
R3	$r_3 = k_3 C_{C_6H_6O_2}$	$k_3 = 7.94\text{x}10^{10}\exp(-226354/RT)$
R4	$r_4 = k_4 C_{C_6H_6O_2}$	$k_4 = 5.01\text{x}10^{14}\exp(-310871/RT)$
R5	$r_5 = k_5 C_{C_6H_6O}$	$k_5 = 1\text{x}10^{11}\exp(-209000/RT_p)$
R6	$r_6 = k_6 C_{C_6H_6O_2}$	$k_6 = 2.51\text{x}10^{12}\exp(-352711/RT)$
R7	$r_7 = k_7 C^2_{C_5H_6}$	$k_7 = 2\text{x}10^{7}\exp(-2013/T)$
R8	$r_8 = k_8 C^2_{C_{10}H_8}$	$k_8 = 4.55\text{x}10^{-4}T^{3.3}\exp(-5690/T)$
R9	$r_9 = k_9 C_{C_8H_8O}$	$k_9 = 1.13\text{x}10^{6}\exp(-109000/RT)$
R10	$r_{10} = k_{10} C_{C_9H_8} C_{C_5H_6}$	$k_{10} = 1\text{x}10^{2}\exp(-33500/RT)$
R11	$r_{11} = k_{11} C_{C_{10}H_8}$	$k_{11} = 1\text{x}10^{11}\exp(-324000/RT)$
R12	$r_{12} = k_{12} C_{C_6H_6} C_{O_2}$	$k_{12} = 1.58\text{x}10^{12}\exp(-202641/RT)$

4.3 Simulation of the gasification process

The gasification process was simulated by changing the equivalence ratio (ER) values of 0.16, 0.17, 0.23 and 0.3. These specific ER values were chosen based on the reported experimental data availability. Corresponding air flow, fuel flow, pyrolysis zone bed height and temperature profile along the pyrolysis zone were taken from reported experimental data as presented in Table 4 and Table 5 [22].

Table 5: Input parameters for the Aspen Plus model

Equivalence Ratio	0.16	0.17	0.23	0.3
Air flow (m^3/h)	10	17	15	12
Fuel flow (kg/h)	14.6	24	16	9.6
Bed height (cm)	13	7	13	13

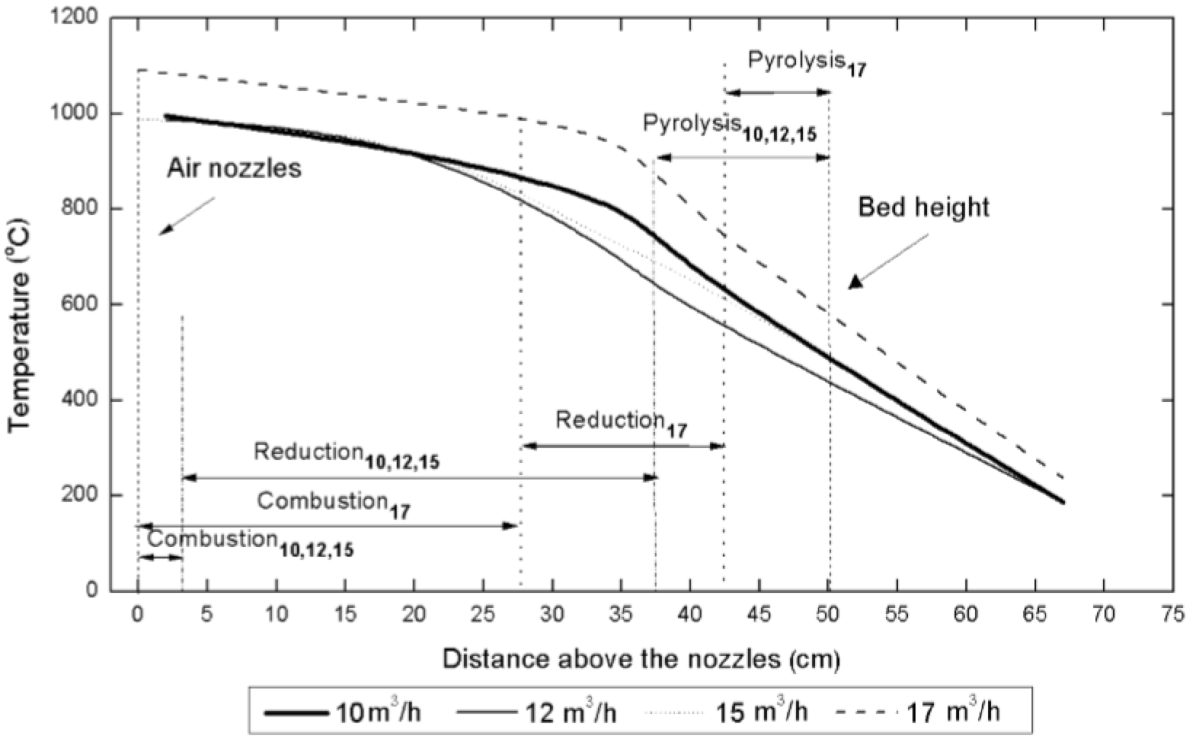


Figure 6: Characteristic of temperature profile in the gasifier

Chapter 5: Results and discussion

5.1 Model validation

The developed model was validated by comparing gas composition and total tar content with reported experimental values from an updraft gasifier in the literature [28].

Table 6 shows the comparison of the simulated composition of syngas with experimental data.

Table 6: Experimental data vs simulated data when ER=0.16

Component	**Experimental data for ER 0.16 (%Volume)**	**Simulated data for ER 0.16 (%Volume)**
CO	28	25
CO_2	8	18
H_2	7	8

According to the simulated data, the prediction of CO and H_2 components are more accurate but CO_2 content is somewhat overestimated.

Table 7 shows comparison of simulated total tar content with experimental data.

Table 7: Experimental total tar content vs simulated data

Tar content	**Experimental data**	**Simulated data**
	50 -100 g/Nm^3	77 -110 g/Nm^3

The total tar content of typical updraft gasifiers reported between 50-100 g/Nm^3 [28]. It is observed that the total tar content in simulated results are only slightly higher than the experiment data and are within the acceptable range. It should be noted that oxidation reactions of Catechol and Salicylaldehyde were not incorporated in the model due to limited kinetic data.

Incorporation of those reactions may reduce the simulated tar content. Further, many parameters such as particle size, moisture content of biomass can also affect the tar formation which was not considered in the model.

5.2 Variation of total tar content with bed height

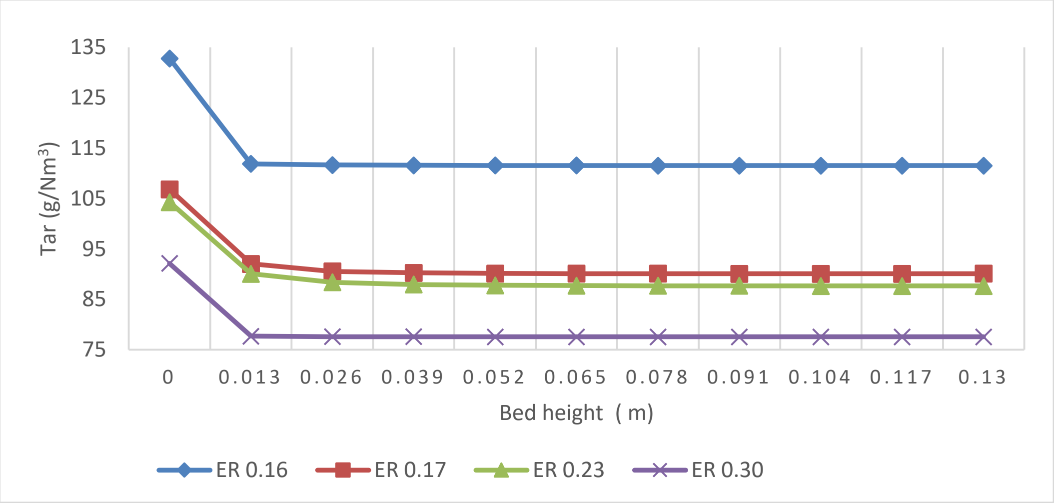


Figure 7: Total tar composition vs bed height

According to Figure 7, it can be observed that the higher tar formation is occurring when ER is 0.16 and the tar content is reducing with the increase of ER. This is because high air flow rates can effectively crack or reform the primary tar. When the ER is 0.30, the temperature in the pyrolysis zone is high which is favorable for tar thermal cracking.

The total tar content is almost constant beyond 1.3 cm bed height in the pyrolysis zone for all the ER values studied. This suggests that, beyond 1.3 cm height in the pyrolysis zone, the formation of tar is not affected by the residence time. At this point, the temperature drops below 600 ^oC which is not favorable for further thermal cracking of tar [22].

5.3 Variation of tar composition with bed height and ER

1. *Equivalence Ratio = 0.16*

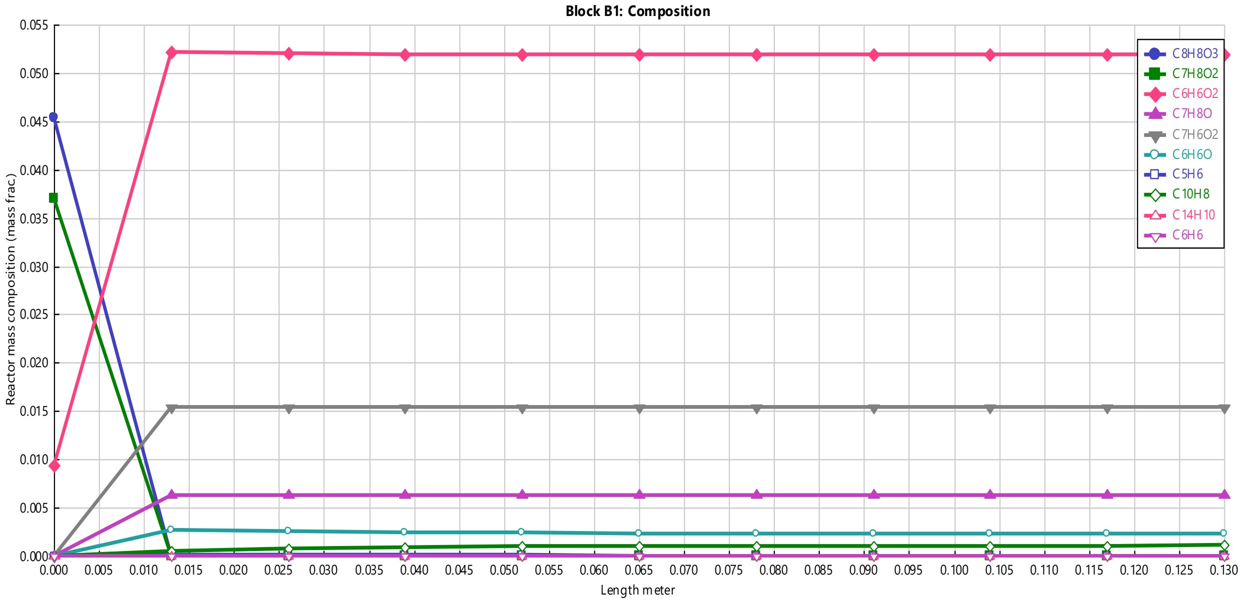


Figure 8: Tar composition at ER=0.16

2. *Equivalence Ratio = 0.17*

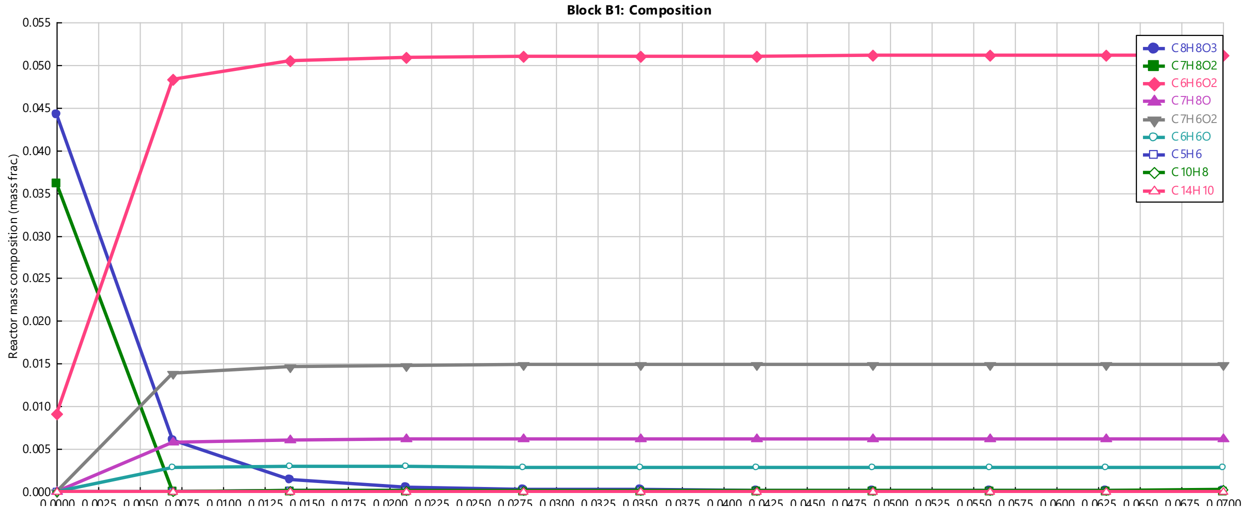


Figure 9: Tar composition at ER=0.17

3. *Equivalence Ratio = 0.23*

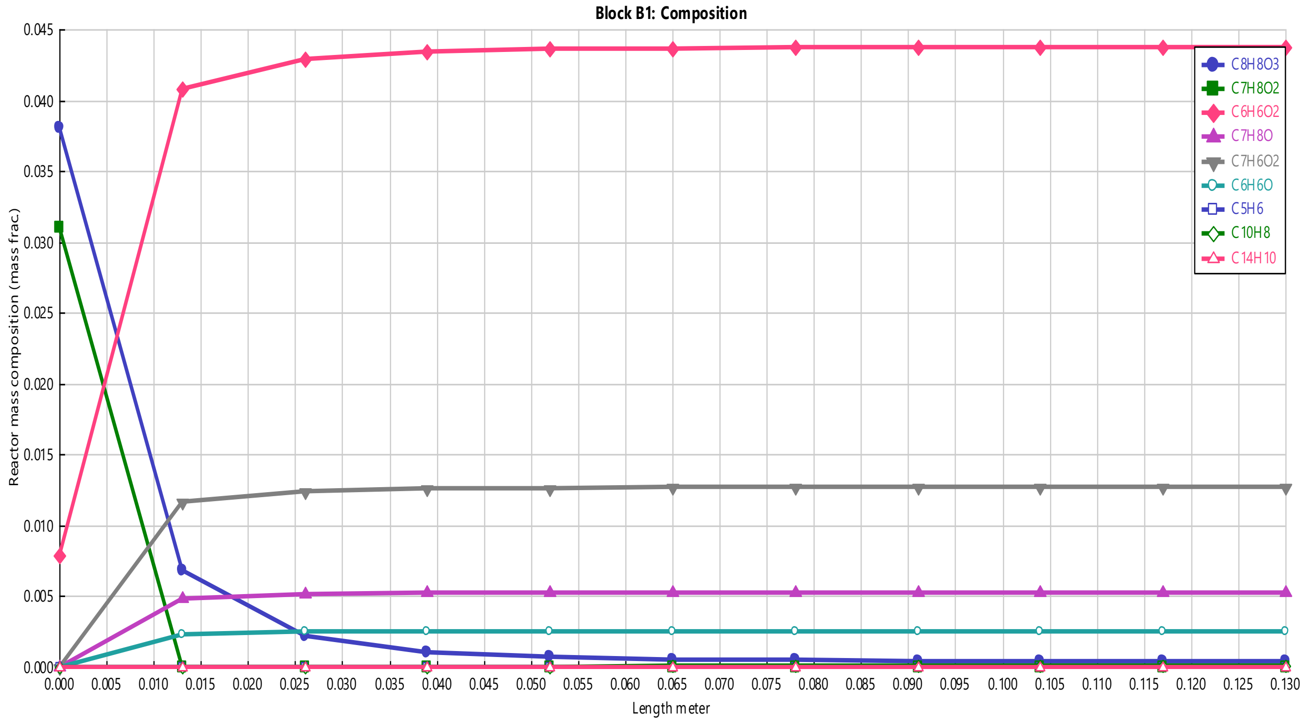


Figure 10: Tar composition at ER=0.

4. *Equivalence Ratio = 0.30*

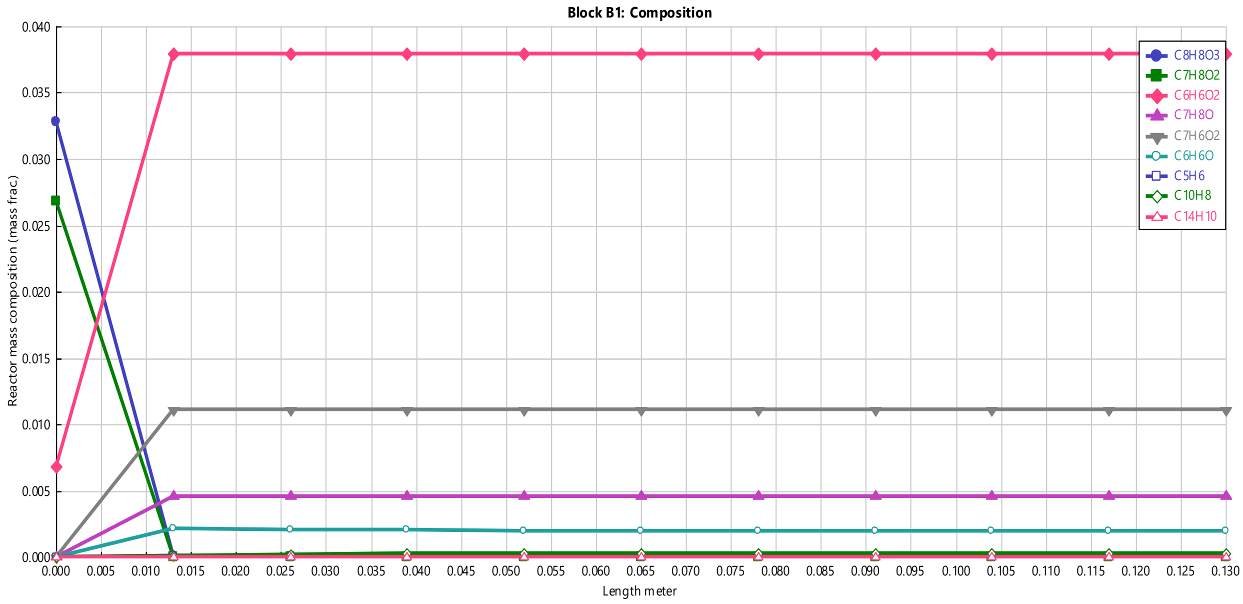


Figure 11: Tar composition at ER=0.30

From Figure 8 to Figure 11 represent variation of mass fractions of tar components along the pyrolysis zone bed height for each ER studied.

Lignin is mainly decomposed into $C_7H_8O_2$ (Guaiacol) and $C_8H_8O_3$ (Vanillin) and $C_6H_6O_2$ (Catechol). These three components were considered as the initial reactants in the complex reaction series [10].

When comparing the curves of mass fractions related to $C_7H_8O_2$ (Guaiacol) and $C_8H_8O_3$ (Vanillin) the curve which represents $C_6H_6O_2$ (Catechol) has a different shape. Because $C_6H_6O_2$ (Catechol) also belongs to primary tar, according to the reaction R2, $C_6H_6O_2$ (Catechol) is a pyrolysis product which is formed from $C_7H_8O_2$ (Guaiacol). With the bed height is increasing, the mass fraction of $C_6H_6O_2$ (Catechol) is tending to increase. It has been reported that the temperatures greater than 1223 K necessary to decompose Catechol into Benzene, Naphthalene, and Phenanthrene owing to the relatively high activation energies of R3, R4 and R6 [4]. Typically, this temperature cannot be achieved in the pyrolysis zone of updraft gasifiers. Further, combustion reaction of Catechol was not included in the model due to lack of kinetics, which also affects the Catechol content.

$C_7H_8O_2$ (Guaiacol) and $C_8H_8O_3$ (Vanillin) are rapidly decomposed. The composition of $C_7H_8O_2$ (Guaiacol) and $C_8H_8O_3$ (Vanillin) have become nearly zero along the bed height. This is because of the thermal cracking, steam reforming, dry reforming, carbon formation and partially oxidation reactions happening while the gasification process is occurring (R1, R2 and R9).

According to the simulation, the major tar compound produced is Salicylaldehyde ($C_7H_6O_2$). Along the bed height until 1.3 cm the production of Salicylaldehyde increases rapidly, followed by a slow increase afterwards. Combustion, pyrolysis and gasification reactions of $C_7H_6O_2$ were not included in the model due to lack of kinetics and it has resulted in this high $C_7H_6O_2$ content.

C_6H_6O (Phenol) is a typical tar component in biomass gasification, and it belongs to secondary tar components. The production of Phenol is decreasing with the increasing ER value. But when considering the bed height, the composition of phenol is progressively increasing along the bed height until about 1.3 cm and after passing 1.3 cm of the beg height the mass fraction of phenol is stable.

When considering the increasing ER value, the production of o-Cresol (C_7H_8O) is also getting lower. Similar to Phenol, until the bed height of the reactor 1.3 cm, o-Cresol production is progressively increasing.

The formation of hydrocarbons C_6H_6, C_5H_6, $C_{10}H_8$, $C_{14}H_{10}$, C_9H_8 are negligible compared to the above oxygenated tar components. Naphthalene ($C_{10}H_8$) is the only hydrocarbon present notably at the lowest ER showing an increasing trend with the bed height.

It was observed that with the increase of ER value, the formation of tar becomes lower. And also, when considering the bed height, after reaching a specific height all the tar components get stable. It can be assumed that the mass fraction of tar is saturated after a specific bed height.

When comparing the values obtained by simulation and the experimental data in the literature using the gas chromatography, some tar components cannot be identified in the simulation. However, the model can be further improved to get such an accuracy by incorporating all the intermediate reactions.

5.4 Variation of total tar content with ER

Figure 12: Total tar composition vs ER

According to the Figure 12, the total tar content is decreasing with increasing equivalence ratio (ER) [29]. This is because, with more oxygen, the formation of tar is getting lower due to oxidation of tar according to R8 and R12 as well as thermal cracking of tar due to high temperature.

5.5 Variation of tar composition with ER

1) According to the Figure 13 to Figure 16, with the ER value is getting higher, the tar compositions of $C_7H_6O_2$, $C_6H_6O_2$, C_7H_8O and C_6H_6O are decreasing. These oxygenated components are getting thermally cracked or hydrogenated according to the R3-R6 reactions forming hydrocarbons. Compared to those tar compounds C_6H_6O (Phenol) is more thermally stable and hence there is no significant destruction until ER of 0.3.

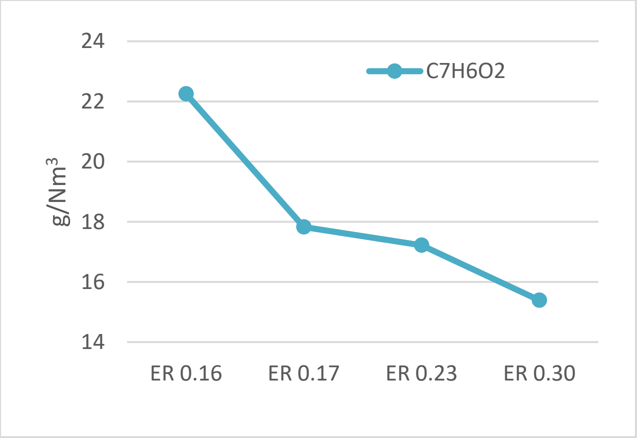


Figure 13: Composition of $C_7H_6O_2$

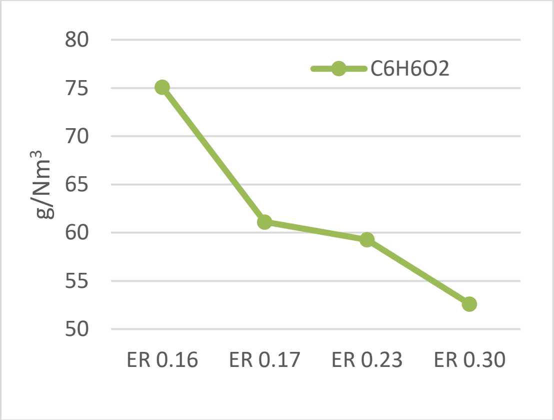


Figure 14: Composition of $C_6H_6O_2$

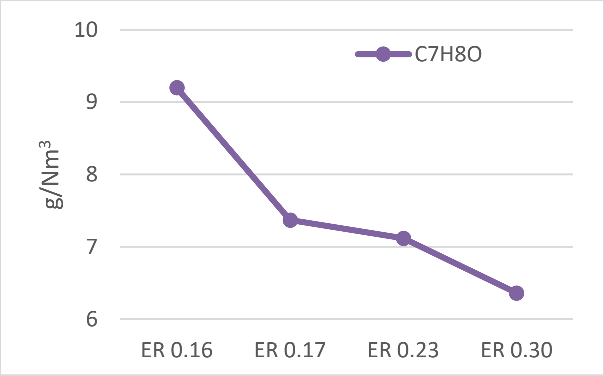


Figure 15: Composition of C_7H_80

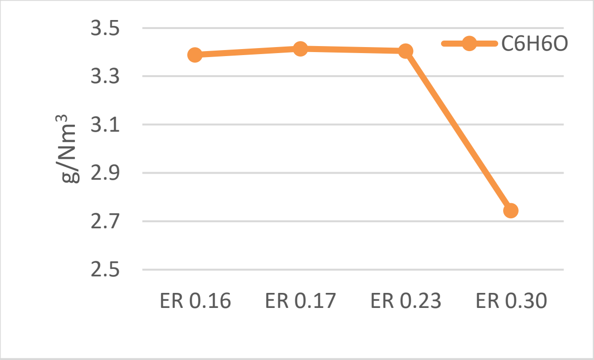


Figure 16: Composition of C_6H_6O

2) According to the Figure 17 to Figure 20, with the ER value is getting higher, the tar composition of $C_{10}H_8$, $C_{14}H_{10}$, C_6H_6 and C_5H_6 are decreasing with a minimum at ER of 0.23, followed by a slight increase. These hydrocarbons are getting cracked with O_2 or reformed with H_2O according to the R8, R11 and R12 reactions forming smaller molecules and gases. The slight increase at ER of 0.3 can be due to cracking and hydrogenation of oxygenates according to R3-R6 resulting the formation of these hydrocarbons. Naphthalene ($C_{10}H_8$) is the only hydrocarbon present in significant amount.

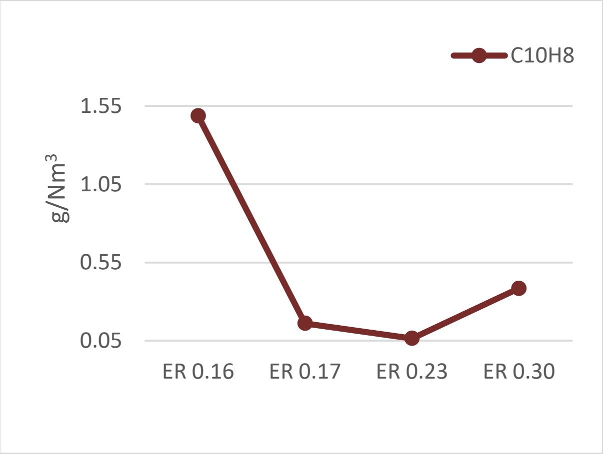


Figure 17: Composition of $C_{10}H_8$

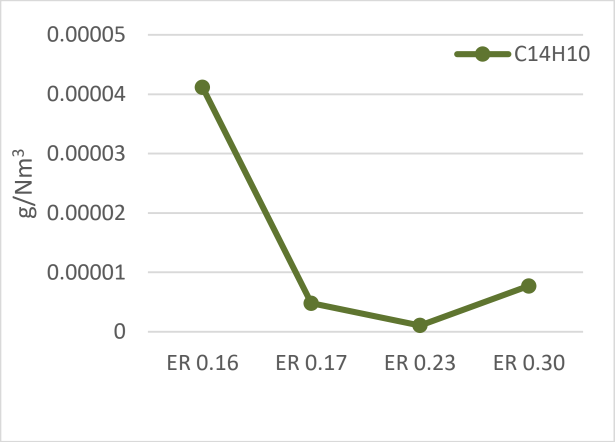


Figure 18: Composition OF $C_{14}H_{10}$

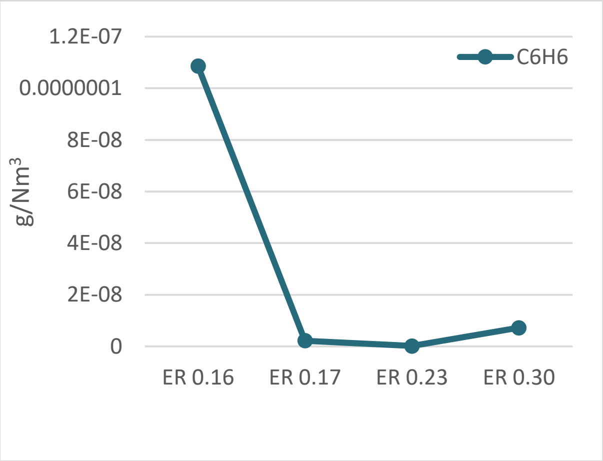


Figure 19: Composition of C_6H_6

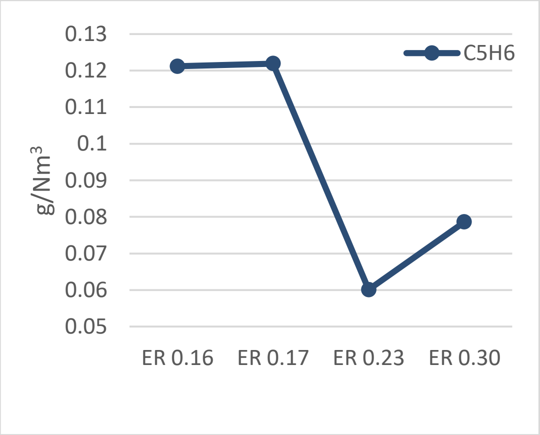


Figure 20: Composition of C_5H

3) According to the Figure 21 and Figure 22, with the ER value is getting higher, the tar composition of $C_7H_8O_2$ and $C_8H_8O_3$ are increasing from zero maximizing at ER of 0.23 and drops to zero again with further increase of ER. These components are lignin constituents. Comparatively low activation energy of R1, R2 and R9 results in prompt destruction of these components even at low ER values.

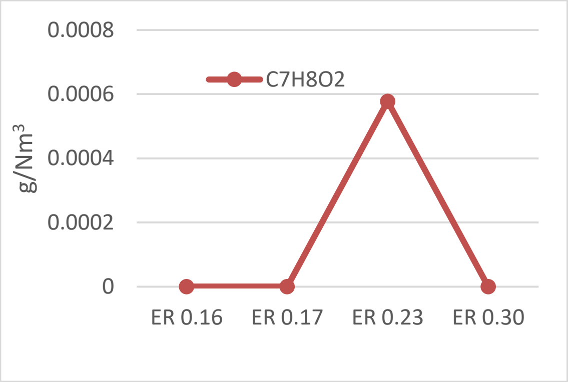


Figure 21: Composition of $C_7H_8O_2$

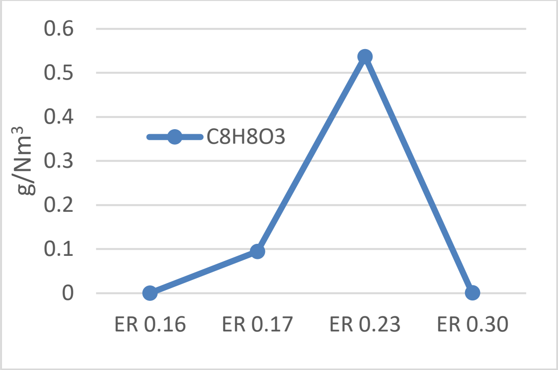


Figure 22: Composition of $C_8H_80_3$

4) According to the Figure 23, with the ER value is getting higher, the tar composition of C_9H_8 is increasing from zero. According to the reaction R8, $C_{10}H_8$ reacts with oxygen to form C_9H_8. Higer ER means that the oxygen flow is higher. Therefor more C_9H_8 is formed.

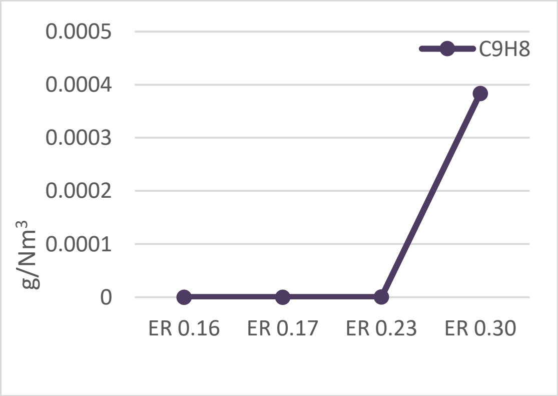


Figure 23: Composition of C_9H_8

5.6 Variation of syngas composition with ER

During the gasification process, the main produced gases are considered as H_2, CO and CO_2. According to the Figure 24, with the increase of ER, the molar fractions of CO and H_2 in the syngas are decreasing and the molar fraction of CO_2 is increasing resulting low heating value at higher ER. This is due to the fact that the O_2 content of the supplying air is accelerating the formation of CO_2 by combustion of carbon in the fuel. Further, tar cracking reactions R4, R8 and R9 are also forming CO_2.

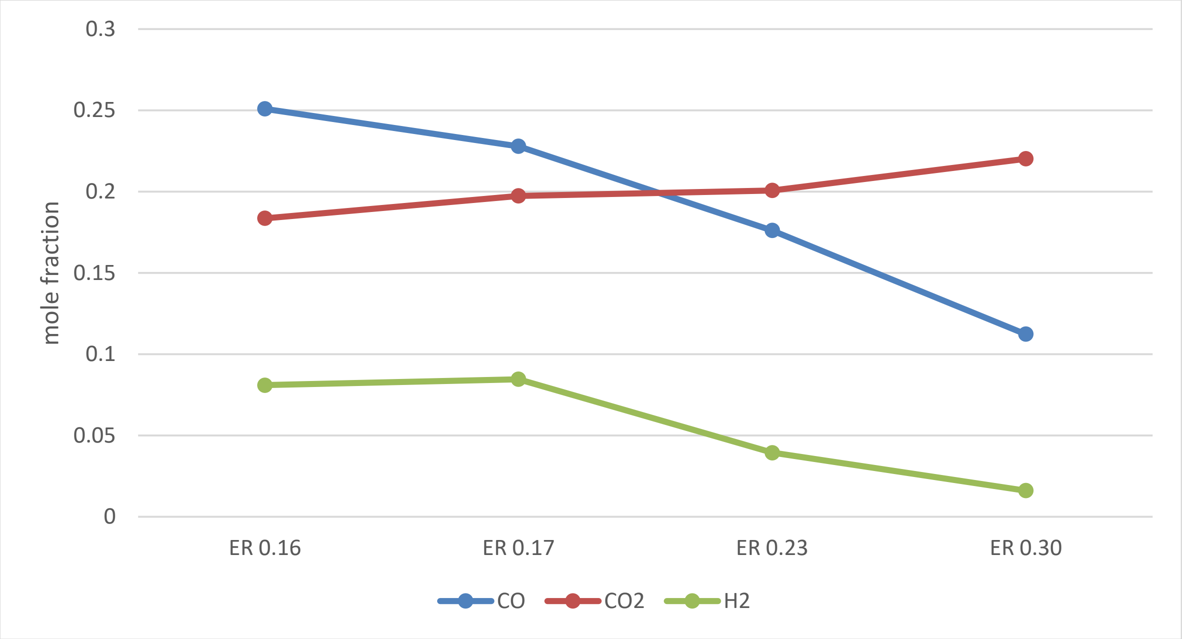


Figure 24: Syngas composition

Chapter 6: Conclusion

During the conversion process of biomass into Bioenergy by using gasification, the formation of tar is the major issue due to tar condensation. It results in increased fouling in the gas cooler and blockage of the pipes of the gasifier. As a result, the maintenance cost can become higher. Therefore, in this study, the tar formation and destruction in an updraft gasifier was studied by developing a kinetic model using Aspen plus 10.0 with the ultimate aim to limit the tar formation by improving the gasifier design as well as operating conditions. Following conclusions can be drawn.

- According to the kinetic model developed for the updraft gasifier studied, the major tar constituents are the oxygenates. Other than that, the only considerable tar component is Naphthalene which is formed significantly at the lowest ER.
- With the increase of ER value, the formation of the tar is decreasing as expected. Based on this, it can be concluded that the temperature is a major factor for the tar cracking in an updraft gasifier. Therefore, by controlling the air supply, the tar formation can be limited. However, the heating value of gas is decreasing with the increase of ER due to prevailing combustion reactions and it is always a trade-off.
- Even if the ER value shows a considerable influence on the tar formation in the updraft gasifier studied, the bed height of the pyrolysis zone has no significant effect on the total tar formation. When the pyrolysis zone bed height exceeds 1.3 cm, the formation of tar is getting stable. Therefore, the bed height is not a main factor affecting the formation for tar. Based on this, it can be concluded that the residence time is not a major factor for the tar cracking in an updraft gasifier.
- The developed model can be used as a guide to optimize the gasifier design and operating conditions such that tar formation and condensation problems are minimized in updraft gasifiers.
- In future, the model can be further improved by considering the cellulose and hemicellulose also as tar forming precursors and incorporating more tar formation and destruction reactions. Further, the effect of moisture content of biomass on the tar yield and composition can also be studied considering the steam reforming reactions of tar.

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