



# Lignocellulose thermal pretreatment and its effect on fuel properties and composition of the condensable products (tar precursors) from char devolatilization for coal substitution in gasification application

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## ARTICLE INFO

### Keywords:

Biomass  
Coal  
Char  
Pyrolysis  
Volatile analysis  
TGA

## ABSTRACT

To establish the potential of thermally pretreated biomass as fuel for coal replacement in applications such as gasification, the fuel properties (higher heating value, elemental and proximate analyses) and the composition of char devolatilization products were analyzed and compared to those of sub-bituminous coal. Samples of pine, bamboo, corn cob and corn stover were pretreated at 250, 300, 350 and 400 °C with a hold time of 30 min. The devolatilization experiments were done in a Thermogravimetric analyzer, while captured volatiles were analyzed by thermal desorption/gas chromatography–mass spectrometry. The results showed that an increase in pretreatment temperature consistently decreased the oxygen and volatile matter contents of the char, while its fixed carbon content and the higher heating values increased, with a more drastic evolution from 300 °C onwards. Analysis of the char devolatilization products confirmed a major modification of the polysaccharides structure, as only traces of depolymerisation products were observed following pretreatment at 350 °C. Devolatilization of chars pretreated at 350 and 400 °C resulted in the evolution of the tar precursors, especially the phenolics, at similar and lower amounts, respectively, in comparison to coal devolatilization. Overall, a pretreatment temperature of at least 350 °C would be recommended for sub-bituminous coal substitution in gasification, while 400 °C could be considered for biomass species with high lignin content.

## 1. Introduction

Fossil based fuels continue to be major sources of the world's energy supply. However such fuels are non-renewable and their quantities are currently on the decline due to increased growth in global industrialization. The use of fossil-based fuels is also known to release high levels of greenhouse gases such as CO<sub>2</sub> and other pollutant emissions into the environment, leading to global warming and other environmental issues such as SO<sub>x</sub> and NO<sub>x</sub> air pollution [1]. On the other hand, lignocellulosic biomass is a renewable source of energy and is considered to be environmentally friendly due to its CO<sub>2</sub> neutrality and low contents of S and N elements, in comparison to fossil-based fuels [2, 3].

Thermochemical processes such as combustion, pyrolysis and gasification are used to convert materials like biomass and coal into energy and fuel products [4, 5]. Among these thermochemical processes, gasification is more efficient and is considered to be one of the promising routes for utilizing coal and biomass on a large scale [6–8]. Fuel gas is the main product of gasification and can be combusted directly in gas

turbines and gas engines for the generation of electricity or upgraded to syngas for conversion into chemicals and liquid fuels through Fischer-Tropsch synthesis [7]. Coal gasification is an already mature technology, while the gasification of biomass is still under development. In order to reduce greenhouse gas emissions from coal and take advantage of the environmental benefits from the use of biomass, recent research on gasification has been focused on the co-utilization of coal and biomass [9, 10]. It has been shown that the addition of biomass to coal during gasification can result in significant increase in the yield of gas due to the high volatile content of biomass [9–11]. However, in addition to the gas there is also an increased production of oxygenated volatile compounds (tar precursors) during the biomass devolatilization steps, which impacts negatively on the quality of the syngas product. The production of such oxygenates, in particular phenolic volatiles, needs to be limited, due to problems associated with their thermal stability and potential to recombine [12]. Such biomass tar condensation leads to the blockage and fouling of process equipment and catalyst deactivation during syngas production and conversion [7, 8, 13]. The problem of tar removal from syngas is therefore a challenge that needs

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<https://doi.org/10.1016/j.fuproc.2018.07.015>

Received 19 March 2018; Received in revised form 1 July 2018; Accepted 17 July 2018

Available online 26 July 2018

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to be overcome to ensure effective utilization of biomass in gasification. Traditionally processes such as the use of electrostatic precipitators, granular beds and scrubbers have been employed to deal with the tar problem. Others include thermal cracking, catalytic cracking and plasma methods but these are expensive and energy intensive methods [7]. In the case of tar scrubbing there is also the production of contaminated water which needs proper disposal thereby adding to the cost [7].

Given the increase in the demand for renewable energy, there is a need to limit the formation of tar precursors during the devolatilization (pyrolysis) step of the biomass-coal co-gasification process. One preferred approach to this consists in pretreating biomass to alter its properties to be closer to that of coal. This will ensure more efficient gasification of the two fuels and in addition limit the problem of tar/oxygenated volatiles generation during devolatilization. Among the processes used to pretreat biomass for energy conversion applications are torrefaction and slow pyrolysis [14]. These two thermal pretreatment processes are carried out at temperatures of 200–300 °C for torrefaction [15, 16] and between 300 and 500 °C for slow pyrolysis [17], both in an inert atmosphere and at low heating rates (< 50 °C/min). During thermal pretreatment of biomass, a significant part of the volatile matter is released from the sample, resulting in a solid product (char) with several improved characteristics such as lower moisture content [14, 18], increased energy density [19], improved grindability [15, 20], hydrophobicity [21, 22], reduced oxygen content leading to lower O/C ratio [23] and a homogeneous solid fuel product [24]. Though several studies have been done on biomass thermal pretreatment, most of these focused on the effect of the pretreatment process on the physico-chemical properties of the char. Studies on the subsequent conversion of the char are limited and need to be explored further especially if char is to be used for coal substitution in gasification applications. Since devolatilization/pyrolysis is a critical step of gasification during which volatiles/tar are generated, it is important to quantify/characterise the devolatilization products generated during the conversion of char for comparison with coal.

In this study torrefaction/slow pyrolysis as thermal pretreatment method is applied to lignocellulosic biomass, with the aim of producing char with improved properties for co-gasification with coal, both in terms of composition of devolatilization products and its fuel properties (composition and energy content). A series of thermal pretreatment experiments were performed on four biomass feedstocks (pine, bamboo, corn cob and corn stover) at temperatures between 250 and 400 °C. Chars and coal were devolatilized/pyrolyzed and the volatiles products were quantified using a recently developed method coupling thermogravimetric analysis and analysis of the captured volatiles by thermal desorption/gas chromatography – mass spectroscopy [25], particularly adapted for the quantification of small amounts of organic volatile products for comparison purpose. In addition, chars were compared to coal in terms of fuel properties such as proximate analysis, elemental composition and higher heating value.

## 2. Materials and methods

### 2.1. Feedstock

The coal used in this study was a typical South African low grade sub-bituminous coal with a relatively high ash content. Prior to its use, the coal was pulverized and then sieved to a particle size range of 160–450 µm (vibratory sieve shaker – model AS200). The biomass feedstocks used were two corn (*Zea mays*) residues; corn stover (CS) and corn cob (CC), pine (*Pinus radiata*) (PN) and bamboo (*Bambusa balcooa*) (BB), which were sourced from the Northern, Eastern and Western provinces, respectively. CC and CS are major agricultural residues produced in large quantities in South Africa [26], while PN is also widely available in South Africa. Also, as a fast growing specie, BB is often considered for energy applications [27] and thus was selected for

**Table 1**

Lignocellulosic composition (wt% daf: dry ash-free basis) of biomass feedstocks.

Component	Feedstock			
	Pine (PN)	Bamboo (BB)	Corn cob (CC)	Corn stover (CS)
Lignin	29.87	25.48	17.76	16.53
Cellulose	40.94	39.39	34.34	36.70
Hemicelluloses	11.82	16.34	26.02	21.28
Extractives	5.19	12.96	10.49	17.53
Acetyl	1.89	3.32	3.91	3.06

this study. All biomass feedstocks were dried to < 10 wt% moisture content and were milled and sieved to 250–450 µm particle size range by means of Retsch mill (model ZM100) and a vibratory sieve shaker (model AS200). Table 1 lists the lignocellulosic chemical composition of the biomass feedstocks as determined by use of the standard laboratory analytical procedures (LAPs) 002, 003, 017 and 019 of the National Renewable Energy Laboratory (NREL) ([http://www.nrel.gov/biomass/analytical\\_procedures.html](http://www.nrel.gov/biomass/analytical_procedures.html)). The standard method DD CEN/TS 14780:2005 was used to obtain sub-samples of each feedstock.

### 2.2. Thermal pretreatment

Torrefaction or slow pyrolysis thermal pretreatment of biomass feedstocks was performed in a TGA (TGA/DSC 1-LF1100 system, Mettler Toledo). Approximately 180–400 mg mass of raw biomass (depending on biomass bulk density) was used for each pretreatment. Thermal pretreatment was done as follows: dynamic heating at 10 °C/min from 30 °C to the appropriate pretreatment temperature (250, 300, 350, and 400 °C), followed by isothermal condition for a hold time of 30 min. Argon (baseline 5.0, Afrox SA) at a flow rate of 70 ml/min was used to provide an inert atmosphere during pretreatment. Pretreatment was performed in triplicate runs and the generated char product stored for further analysis.

### 2.3. Fuel characterization

Proximate and elemental analyses as well as higher heating value (HHV) determination were performed on coal and raw/thermally treated biomass samples to determine their fuel properties. Proximate analysis was conducted according to the ASTM method E1131, by means of thermogravimetric analysis (TGA) (TGA/DSC 1-LF1100 system, Mettler Toledo) to determine the percentage composition of volatile matter (VM), fixed carbon (FC) and ash in each sample. Elemental analysis (C, H, N, and S) of samples was done using a Leco TruSpec Micro elemental analyzer and O content was determined by difference. HHV was measured by oxygen bomb calorimetry (CAL2K ECO bomb calorimeter – model 2013) and was determined according to the ASTM standard D5865-11a.

### 2.4. Devolatilization and quantitative analysis of condensable volatiles

To study and compare the types and quantities of condensable volatiles generated during devolatilization of coal and biomass (raw/pretreated) samples, a method coupling thermogravimetric-analysis and thermal desorption/gas chromatography–mass spectrometry (TGA–TD/GC–MS) was used. Details of the analytical method can be found in Nsaful et al. [25]. Samples were pyrolysed in a TGA and evolved volatiles captured into thermal desorption (TD) tube, which were then analyzed offline using a thermal desorber/GC–MS system for the separation, identification and quantification of pyrolysis condensable volatiles.

For devolatilization, a 10 mg sample was pyrolysed in an inert atmosphere from 30 °C to 600 °C at a heating rate of 10 °C/min using a TGA/DSC 1-LF1100 system (Mettler Toledo). Argon (baseline 5.0, Afrox

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