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# Thermochemical Conversion Behavior of Different Biomass Feedstocks: Pyrolysis and Gasification

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**Abstract:** In this study, a bench-scale bubbling fluidized bed (BFB) gasifier and thermogravimetric analyzer (TGA) were applied for the determination of the thermochemical conversion reactivity of biomass fuels under both gasification and pyrolysis conditions. Six different biomass feedstocks, namely; straw pellet (SP), softwood pellet (WP), torrefied wood chips (TWC), pyrolysis char (PC), milled sunflower seed (MSS) and dried distillers' grains and solubles (DDGS) were investigated. TGA of biomass feedstocks were carried out under pyrolysis conditions at four different heating rates (2-15 °C/min). Raw data obtained from the experiments were used to calculate the kinetic parameters (A, $E_a$) of the samples by using two different models; Coats-Redfern and Isoconversional Method. TGA analysis showed that pyrolysis char was the only sample having decomposition temperature above 800 K since it was the pre-pyrolized sample before gasification. According to Derivative Thermogravimetric Analysis (DTG) profiles, two peaks and two shoulders at around 450-650 K were observed for DDGS whereas no peaks were detected for pyrolysis char as the indication of absence of volatiles/cellulosic components. It was seen that the highest devolatilization rates and devolatilization temperatures (associated mainly with cellulose decomposition) were obtained for softwood and torrefied wood samples, which had the least char yields among the other biomass feedstocks. It was seen that WP was more reactive for thermochemical conversion and less prone to agglomeration. Furthermore high ash content and agglomeration index of MSS were the potential drawbacks in front of its utilization via thermochemical conversion. During the air gasification of these feedstocks (except DDGS), the product syngas was characterized in terms of main gas composition, tar, and sulfur compounds. It was shown that the highest cold gas efficiency, carbon conversion and calorific value were obtained for the gasification of SP. On the other hand, SP had some drawbacks regarding its high agglomeration tendency and low deformation temperature. Among all feedstocks, gasification reactivity of MSS was found to be quite poor. MSS seemed to expose to pyrolization instead of gasification. WP and TWC were gasified with acceptable conversion values and efficiencies when compared with SP. It was understood that WP is the preferred choice for the thermochemical conversions.

**Keywords:** Thermochemical conversion; gasification; pyrolysis; syngas; biomass.

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## INTRODUCTION

Biomass can be a generous source for energy, fuels, and chemicals (1, 2). Gasification is a process for converting lignocellulosic biomass and/or agricultural wastes into fuel gases (having BTU of 5-15 $MJ/Nm^3$) using air, air/oxygen, steam, $CO_2$, or their combinations as gasification agents. The syngas produced can be directly utilized as fuels for heat and electricity generation, or as feedstocks for chemical production such as methanol, ethanol, dimethyl ether, and Fischer-Tropsch oils (3). Many studies were conducted to evaluate the efficiency and performance of the biomass gasification process. Gasification characteristics of various types of biomasses were investigated such as: sugarcane residue (4), rice hulls (5), pine sawdust (6), almond (7, 8), wheat straw (9), food waste (10), and wood-based biomass (11). Lignocellulosic biomass is mainly composed of cellulose and hemicellulose (60-80% dry basis), lignin (10-25%), some extractives, minerals, and small amounts of sulfur, nitrogen, and chlorine (12). The amount of these elements varies depending on species and location (13). Three main components of lignocellulosic biomass show different decomposition profiles during pyrolysis. Hemicellulose dehydrates at 90°C and reaches a maximum decomposition rate at around 300 °C whereas cellulose begins to decompose after hemicellulose and reaches a maximum decomposition rate at 400 °C approximately. Lignin has more complex structure than hemicellulose or cellulose, its thermal decomposition occurs between 300 and 600 °C (14). A simplified mechanism for biomass gasification can be represented as follows, consisting of four overlapping aspects (15):

(1) Pyrolysis: Biomass → Char, $H_2$, CO, $CO_2$, $H_2O$, $CH_4$, $C_nH_m$, tars, *etc*.

(2) Tar cracking: Tar → $H_2+CO+CO_2+$*etc.*

(3) Heterogeneous reactions:
$C+1/2O_2 \rightarrow CO$ (Char oxidation)
$C+O_2 \rightarrow CO_2$ (Char oxidation)
$C+CO_2 \leftrightarrow 2CO$ (Boudouard equilibrium)
$C+H_2O \leftrightarrow CO+H_2$ (Heterogeneous water-gas equilibrium)
$C+2H_2 \leftrightarrow CH_4$ (Hydrogasification Equilibrium)

(4) Homogeneous reactions:
$CO+1/2O_2 \rightarrow CO_2$
$H_2+1/2O_2 \rightarrow H_2O$
$CO+H_2O \leftrightarrow CO_2+H_2$ (Water-gas shift)
$C_xH_y+xH_2O \leftrightarrow xCO+(x+y/2)H_2$ (Steam reforming)
$C_xH_y+xCO_2 \leftrightarrow 2xCO+ y/2\ H_2$ (Dry reforming)

It is known that the cellulose, hemicellulose, and lignin amounts in the biomass affect gasification behavior. Yang *et al.* studied hemicellulose, cellulose, and lignin pyrolysis characteristics and reported that lignin contributed to higher $H_2$ yields than cellulose (16). In a study by Kumabe *et al.*, carbon conversion efficiencies for cellulose, hemicelluloses, and lignin were reported as 97.7%, 92.2%, and 52.8%, respectively (11). They also stated that the gasification products were similar for lignin and hemicelluloses, whereas cellulose produced higher amounts of $CO_2$

and $CH_4$ in the product gas. Kezhong *et al.* co-gasified Shenmu coal with pine sawdust and rice straw, and they found out that $H_2$ composition in syngas increased from 17.66% for pine sawdust to 21.96% for rice straw (17). Herguido *et al*. investigated the steam gasification behavior of different lignocellulosic residues. According to their results, syngas composition varied with the biomass type and gasification temperature (18). There are many factors influencing thermochemical conversion process: (a) intrinsic biomass characteristics such as moisture content, carbohydrate and ash compositions, bulk density, and particle size/shape distributions (b) thermochemical conversion system design and operation conditions like steam to biomass ratio, equivalence ratio, heating rate, temperature profile of the reactor and heat input. This first group of factors determines the reactivity of the biomass and can impact the economics of transforming biomass into value-added products. The aim of this study is to compare the thermochemical conversion reactivity of six different biomass samples, namely straw pellet, softwood pellet, torrefied wood chips, pyrolysis char, milled sunflower seed and dried distillers' grains and solubles (DDGS). For this purpose, all samples were chemically characterized to identify the samples. Then, their gasification tendencies (except DDGS) and pyrolysis behavior were investigated via using bubbling fluidized bed gasifier test unit and thermogravimetric analyzer, respectively.

## MATERIALS AND METHODS

### Characterization of the biomass feedstocks

The straw pellet (SP), softwood pellet (WP), torrefied wood chip (TWC), pyrolysis char (PC), milled sunflower seeds (MSS) and dried distillers' grains and solubles (DDGS) were supplied in the scope of "The European Research Infrastructure for Thermochemical Biomass Conversion (BRISK)" project funded by European Commission Seventh Framework Programme. Before analysis, the raw materials were prepared by grinding and sieving the samples below 250 µm. Proximate and ultimate analyses of the samples were conducted according to the relevant American Society for Testing and Materials (ASTM) standards. Their lower and higher heating values both on original and dry basis were measured and calculated as described in ASTM D 5865. Perkin Elmer Optima 2100 Inductively Coupled Plasma (ICP)-OES analyzer and X-Ray Fluorescence were applied to determine the inorganic content of the fuel and agglomeration indexes. Ash melting behaviors of the samples (initial deformation, softening, hemispherical, and fluid temperatures of ashes) were analyzed by LECO AF700 Ash Fusion Determinator.

### Pyrolysis experiments of biomass feedstocks by TGA

Thermogravimetric analysis of biomass feedstocks have been carried out under pyrolysis conditions by using Mettler Toledo TGA 851 instrument. Experimented TGA conditions are given in Table 1. Raw data obtained from the experiments were used to calculate kinetic parameters (A, $E_a$) of samples by using two different models; Coats-Redfern and Isoconversional method.

**Table 1:** TGA conditions for the pyrolysis of the biomass feedstocks.

| | |
|---|---|
| Initial weight. $m_0$ | ~35 mg |
| $N_2$ flow rate | 40 mL/min |
| Fine powder sample size | <250 µm |
| Heating rate | 2-5-10-15 °C/min |
| Initial-final temperature | 25-850 °C |

**Experimental apparatus: Bubbling fluidized bed gasifier**

The gasification experiments were performed in a 20 $kW_{th}$ atmospheric bubbling fluidized bed gasifier, shown in Figure 1. The gasification reactor made of AISI 310S stainless steel, with a height of 2.29 m and an inner diameter of 82 mm. Four thermocouples, T/C-1, T/C-2, T/C-3 and T/C-4, were installed to measure the temperature at the axis of the reactor. The thermocouples were of type K. Two electrical furnaces were used to heat the reactor. Two screw feeders, positioned one on top of the other, were used to feed the biomass fuel to the reactor. Nitrogen gas at ambient temperature was used to facilitate the fuel feeding. Air, as a gasification agent, was fed to the gasifier at ambient temperature by means of an air compressor. All flow rates were measured/controlled with a rotameter. The particle sizes of SP, WP, TWC, PC, MSS and DDGS were in the range of 0.5–1.0 mm. The fuel feeding rates of the feedstocks, equivalence ratios (ER) and typical operation parameters were given in Table 2. Silica sand (99.2% $SiO_2$, 0.5% $Al_2O_3$ and 0.1% $Na_2O$) was used as the bed material. The bed material had a mean particle size of 450 µm.

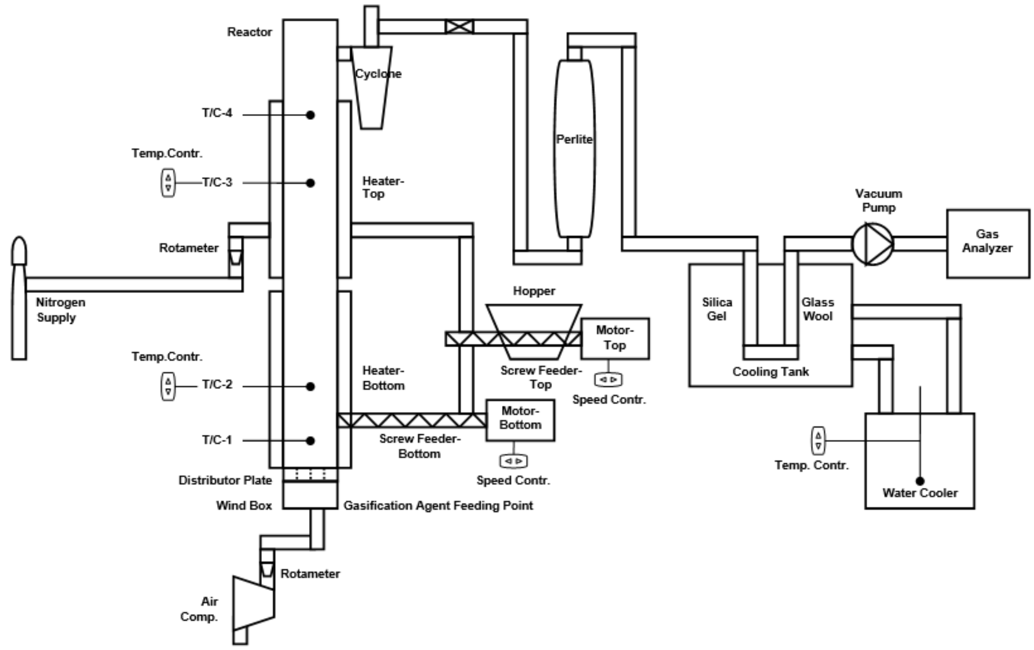


**Figure 1**: The schematic diagram of the bubbling fluidized bed gasifier.

**Table 2:** Typical operation parameters for biomass gasification experiments.

| | **SP** | **WP** | **TWC** | **PC** | **MSS** |
|---|---|---|---|---|---|
| Reactor temperature (°C) | 780 | 760 | 760 | 740 | 760 |
| ER | 0.24 | 0.21 | 0.29 | 0.25 | 0.25 |
| Fuel feeding rate (g/h) | 566 | 581 | 400 | 466 | 490 |

### Syngas characterization

Product gas leaving the gasifier passed from the cyclone where the particulates in the product gas were captured. Two T unions were placed at the cyclone outlet. One of them was connected to a sulfur inert tube, a vacuum pump, and a Tedlar bag. This line was used for sampling of syngas and for measurement of its composition, along with the contaminants like $H_2S$, COS and $NH_3$. EPA 15 Method "Determination of hydrogen sulfide, carbonyl sulfide, and carbon disulfide emissions from stationary sources" was applied and Agilent 6890N gas chromatograph equipped with pulsed flame photometric detector was used to analyze the sulfur-based compounds. Total sulfur content of the gas samples was measured by Analytic Jena multi EA® 5000 UV Fluorescence as well.

Syngas composition (CO, $CO_2$, $H_2$, $CH_4$, and $O_2$) was measured with an ABB AO2040 online gas analyzer. CO, $CO_2$, and $CH_4$ were detected by the non-dispersive infrared absorption technique, whereas hydrogen and oxygen were analyzed with thermal conductivity and paramagnetic detectors, respectively. The $N_2$ component of the product gas is calculated from the balance. The amounts of C1 - C5 hydrocarbon components of the syngas were determined by gas chromatographic measurements equipped with flame ionization detector (FID), by sampling through the Tedlar bags. The second T union at the cyclone outlet was used for tar sampling. Tar compounds were collected according to the tar protocol (DS/CEN/TS 15439). Iso-propanol was used as a solvent for tar trapping. Tar compounds were analyzed by a GC-FID.

## RESULTS AND DISCUSSION

### Biomass Feedstock Characterization

The results of proximate and ultimate analysis together with the higher heating values of the samples are given in Table 3. As it is seen in the table, PC has the highest fixed carbon and the lowest volatile matter content amongst the others, which is the indicative of its pyrolized nature. WP and SP are seen to have nearly the same amount of moisture and fixed carbon. On the other hand, the fixed carbon content of torrefied wood chips was 8% higher than that of WP as expected due to the release of its volatile matter upon torrefaction. Regarding the ash, wood was distinguished with its low ash content while MSS and DDGS were the ash-rich samples among the others. It is known that woody samples usually contains relatively low amount of ash while straw, bark, grasses and grain have significantly higher ash contents [19].

Tables 4, 5 and 6 show the chemical analysis of the ash, ash melting temperatures and calculated agglomeration indexes for all samples, respectively. It is known that high levels of alkali/alkaline metals and chlorine content are responsible for fouling, corrosion, sintering and agglomeration during combustion and gasification processes (20). It was seen in the Tables that MSS and DDGS have higher amounts of alkali and alkaline earth metals (K, Na, Ca, *etc.*) than the others, which react with silica to form alkali and alkaline earth metal silicates with low melting temperatures.

When the fuel analysis results of the samples were compared, SP, MSS and DDGS were the samples with relatively high ash content. On the other hand, in terms of agglomeration index of (Si+P+K)/(Ca+Mg), these samples seemed to be more prone to agglomeration during thermochemical conversion as well. The lowest ash fusion temperatures of these samples supported its agglomeration tendency. This is thereof high $Na_2O$ and $K_2O$ contents of their ash.

**Table 3:** Proximate and ultimate analysis and heating values of the biomass feedstocks.

| | **SP** | **WP** | **TWC** | **PC** | **MSS** | **DDGS** |
|---|---|---|---|---|---|---|
| **PROXIMATE ANALYSIS (wt.%)** | | | | | | |
| **Original Basis** | | | | | | |
| Moisture | 7.40 | 7.52 | 5.58 | 2.16 | 8.42 | 6.88 |
| Volatile matter | 70.50 | 76.85 | 71.53 | 20.27 | 66.36 | 71.50 |
| Ash | 5.85 | 0.53 | 0.17 | 2.17 | 7.44 | 6.14 |
| Fixed carbon | 16.25 | 15.11 | 22.73 | 75.40 | 17.78 | 15.50 |
| **Dry Basis** | | | | | | |
| Volatile matter | 76.13 | 83.09 | 75.75 | 20.71 | 72.46 | 76.77 |
| Ash | 6.32 | 0.57 | 0.18 | 2.21 | 8.12 | 6.59 |
| Fixed carbon | 17.55 | 16.34 | 24.07 | 77.07 | 19.42 | 16.64 |
| **ULTIMATE ANALYSIS (dry basis, wt.%)** | | | | | | |
| C | 49.52 | 54.30 | 58.66 | 87.53 | 48.86 | 49.02 |
| H | 5.72 | 5.80 | 5.52 | 3.73 | 5.80 | 6.38 |
| N | 0.77 | 0.002 | 0.15 | 0.60 | 4.78 | 5.50 |
| $S_{total}$ | 0.13 | 0.03 | 0.05 | 0.00 | 0.57 | 0.85 |
| O (by difference) | 37.54 | 39.30 | 35.44 | 5.93 | 31.87 | 32.11 |
| **HIGH HEATING VALUES (kcal/kg, (dry basis))** | | | | | | |
| HHV | 4595 | 4791 | 5206 | 7937 | 4540 | 4853 |

**Table 4:** Chemical analysis of the biomass ashes measured by ICP (mg/kg, dry basis).

| | **SP** | **WP** | **TWC** | **PC** | **MSS** | **DDGS** |
|---|---|---|---|---|---|---|
| Al | 22 | 65 | 20 | 259.2 | 1028.8 | 70.1 |
| Ca | 1577 | 1415 | 546 | 3655.3 | 4617.0 | 1510.3 |
| Fe | 68 | 149 | 41 | 744.1 | 724.3 | 191.8 |
| K | 1635 | 299 | 180 | 510.9 | 13130.0 | 14421.4 |
| Mg | 216 | 152 | 100 | 776.1 | 5255.3 | 5487.2 |
| Mn | 6 | 94 | 51 | 90.8 | 203.8 | 106.5 |
| Na | 452 | 125 | 89 | 798.9 | 431.2 | 4347.9 |
| P | 145 | 76 | 26 | 162.9 | 6368.5 | 6289.3 |
| Si | 414 | 307 | 60 | 775.3 | 1127.9 | 589.9 |
| Zn | 0 | 2 | 4 | 67.4 | 149.4 | 111.9 |

**Table 5:** Ash melting temperatures of biomass feedstocks,°C.

| **Feedstock** | **IDT** | **ST** | **HT** | **FT** |
|---|---|---|---|---|
| SP | 955 | 1051 | 1162 | 1256 |
| WP | 1353 | 1425 | 1427 | 1438 |
| TWC | >1500 | >1500 | >1500 | >1500 |
| PC | 1371 | 1379 | 1391 | 1432 |
| MSS | 1127 | 1128 | 1162 | 1375 |
| DDGS | 900 | 900 | 900 | 1220 |

IDT: Initial deformation temperature, ST: Softening temperature, HT: Hemispherical temperature, FT: Fluid temperature

**Table 6:** Agglomeration indexes of the biomass feedstocks (mole/mole).

| | SP | WP | TWC | PC | MSS | DDGS |
|---|---|---|---|---|---|---|
| Si/(Ca+Mg) | 0.26 | 0.31 | 0.12 | 0.22 | 0.12 | 0.08 |
| (Si+P+K)/(Ca+Mg) | 1.27 | 0.51 | 0.43 | 0.37 | 1.75 | 2.25 |

Raveendran *et al.* reported that metals influence pyrolysis and gasification mechanism (14). Alkali metals are good catalysts for carbon-gas reactions. A number of experimental and modeling studies have been conducted to observe and predict ash behavior in gasification systems (23, 24). It was found that the order of retention in the bed for different elements is Ca > K > Mg > P (20). Therefore, the alkali metal content of the samples might have a catalytic function during combustion and gasification.

### Pyrolysis experiments of biomass feedstocks with TGA

Thermal decomposition of biomass is influenced by many factors such as heating rate, temperature, pressure, residence time, moisture, composition, and particle size. In this study, all six biomass feedstocks were pyrolyzed under the conditions given in Table 1. Thermographs were taken at four different heating rates (2-15 °C/min) from 25 to 850 °C under $N_2$ atmosphere. The change of weight loss (TG) and derivative weight loss (DTG) profiles of these feedstocks with heating rates were plotted and evaluated. Effect of heating rate on the TG/DTG profiles for SP was given as an example in Figure 2a and 2b, respectively. The profiles for all other samples can be reached in the conference presentation proceedings (21). It was well established that thermolysis of biomass generally occurs between 200-400 °C. TGA proceeds in three stages for wood: water evaporation, active pyrolysis and passive pyrolysis according to the Gasparovic *et al.* (22). As seen in Figure 2a-b, heating rate affects TG and DTG curve positions, maximum decomposition rate, and location of maximum peaks. When heating rate increases, initial and final temperature of active and passive pyrolysis regions also increase. The maximum points of DTG curves are shifted to higher temperature. For example, the peak for passive pyrolysis region obtained from DTG profile of SP was increased from 302 to 340 °C when the heating rate was increased from 2 °C/min to 15 °C/min (Figure 2b). Nearly the same trend was observed for all feedstocks. Because the temperature intervals of hemicellulose and cellulose decomposition partially overlap each other, the hemicellulose decomposition usually appears as a shoulder instead of a well-defined peak, as was also observed by Gunnar *et al.* (23).

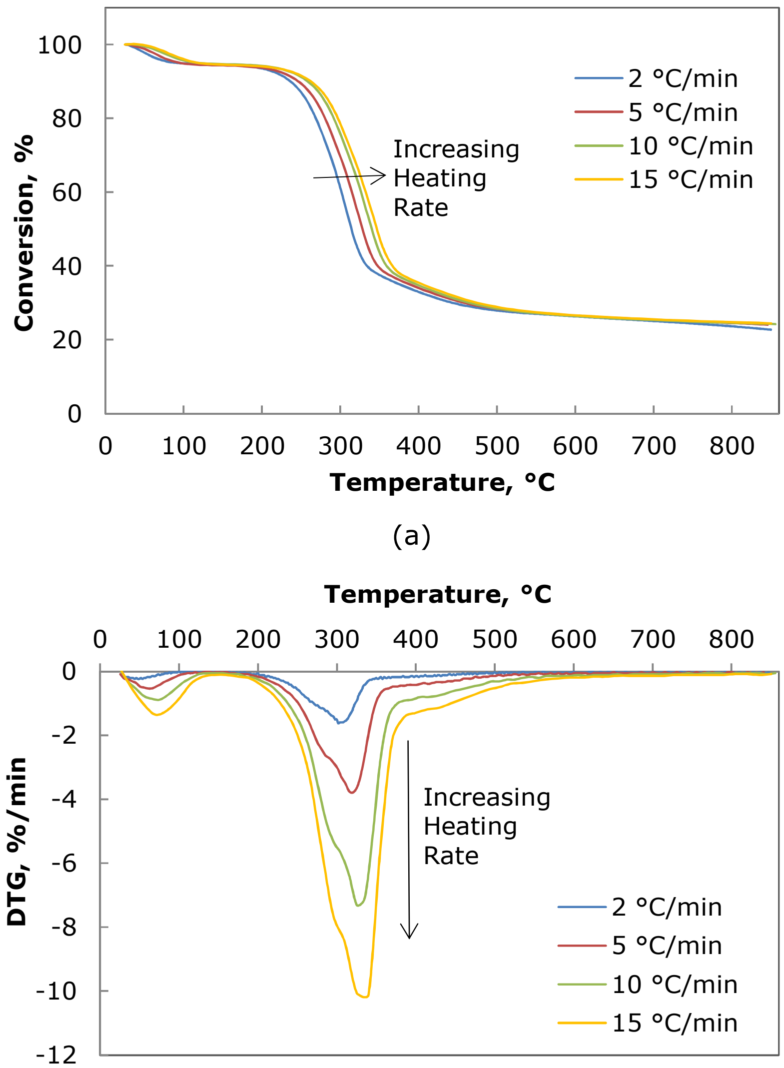
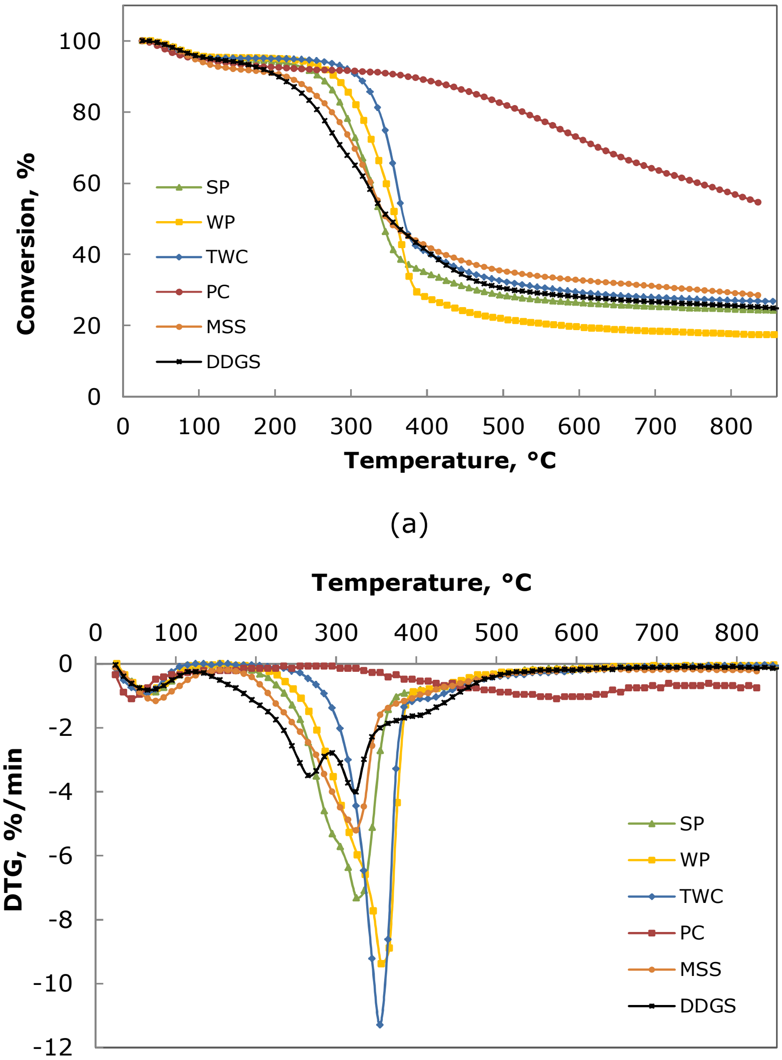


**Figure 2:** Pyrolysis profiles of straw pellet at different heating rates (a) Weight loss curves (b) Derivative weight loss curves.

When the TG and DTG profiles of all feedstocks were plotted on the same scale as in Figure 3a-b, respectively it was seen that the highest devolatilization rates and maximum temperatures (associated mainly with cellulose decomposition) were obtained for TWC and WP. Among all the examined samples, DTG profile of DDGS and PC differed from others. Two peaks and two shoulders at around 165-380 °C were observed for DDGS at 2°C/min while no peaks were detected there for PC as an indication of absence of volatiles/cellulosic components. During the pyrolysis process, PC lost its volatile content. So, PC has no peaks due to its high amount of fixed carbon (~77%).



(a)

(b)

**Figure 3:** Pyrolysis profiles of all biomass feedstocks at 10 °C/min (a) Weight loss curves (b) Derivative weight loss curves.

There are many methods for analyzing non-isothermal solid-state kinetic data from TGA (24-25). These methods can be divided into two types: model-fitting and model-free. Model-fitting methods were widely used for solid-state reactions because of their ability to directly determine the kinetic parameters from a single TGA measurement. However, these methods suffer from several problems, such as their inability to uniquely determine the reaction model, especially for non-isothermal data. On the other hand, the model free methods require several kinetic curves to perform the analysis. Calculations from several curves at different heating rates are performed on the same value of conversion, which allows calculating the activation energy for each conversion point. In this study, the results obtained from TGA were elaborated according to Coats-Redfern (model fitting) and Isoconversional (model free) methods to calculate the kinetic parameters; namely apparent activation energy ($E_a$) and pre-exponential factor (A) of biomass feedstocks. It was seen that the choice on the starting and ending points of decomposition stages was determinative in model fitting methods, whereas model free methods were evaluated to be independent from the choice of the stages and gave more freedom to the user. Thus, evaluations were progressed on the model free methods. The values obtained for pyrolysis char was questionable since the decomposition profiles were in poor quality due to its high fixed carbon content. So PC was disregarded in the evaluations. For isoconversional method, activation energies at 40% and 60-70% conversions, which can be taken as a measure of holocellulose (hemicellulose+cellulose) decomposition, were compared for other five samples (Table 6). Based on the fixed carbon and ash contents of the samples, activation energies were changed as well. In case of TWC, activation energies at 40% and 70% conversions were 189.8 and 377.3 kJ/mole, higher than those values for non-torrefied wood (WP). Similarly, SP gave activation energies changing between 197.8 kJ/mole and 202.4 kJ/mole. It was seen that the lowest activation energies were obtained for WP as an indication of its higher reactivity to thermochemical conversion.

**Table 6:** Activation Energies in kJ/mole at 40% and 60-70% Conversions

| Conversion (%) | Activation Energy (kJ/mole) | | | | |
|---|---|---|---|---|---|
| | **SP** | **WP** | **TWC** | **DDGS** | **MSS** |
| 40 | 197.8 | 172.8 | 189.8 | 238.0 | 186.5 |
| 60-70 | 202.4 | 172.6 | 377.3 | 350.3 | 187.5 |

**Gasification experiments in BFB gasifier**

The syngas compositions obtained during the gasification study were given in Table 7. Calculated gasification yields such as cold gas efficiency, carbon conversion, gas yield and calorific values of the syngas were reported in Table 8. When the results were evaluated, it was seen that MSS produced the highest tar yield (~ 32.8 gC/Nm$^3$), compared with the other biomasses whilst TWC has the lowest tar amount as ~ 1 gC/Nm$^3$. Torrefaction was considered to have an effect on decreasing the tar content. The lowest carbon conversion and cold gas efficiency were obtained with MSS and PC. This was expected for PC since it was the pre-pyrolized sample before the gasification. On the other hand, gasification reactivity of MSS was found to be quite poor. It seemed that MSS was exposed to pyrolization instead of gasification. This might be related to its lower bulk density and poor fluidization conditions inside the gasification reactor. Considerably 10 times less tar was produced during the gasification of torrefied sample (TWC) in relation to its non-torrefied counterpart (WP). Carbon conversions and cold gas efficiencies were also decreased from 69.7% and 56% to 59.1% and 53% upon torrefaction. According to X. Ku *et al.,* intensified energy density of torrefied biomass needs a longer oxidation period, therefore a gasifier for torrefied biomass requires longer gasification zones to reach the same level of conversion (26). Although this was claimed for entrained flow gasification, a similar case might be valid for bubbling bed gasification as well. The tar compounds analysis with respect to biomass feedstock types as shown in Table 9, relatively higher concentrations of lignin-degraded phenolic compounds were present in MSS. It is known that the phenol and benzene derivatives in the tar products were mainly resulted from lignin decomposition by cleavage of its ether linkages at a higher temperature (27). Therefore, this might be the indication of relatively high lignin content of MSS compared to other samples.

**Table 7:** Syngas composition with respect to biomass type.

| | **SP** | **WP** | **TWC** | **PC** | **MSS** |
|---|---|---|---|---|---|
| CO (%) | 11.9 | 12.2 | 7.2 | 9.0 | 8.6 |
| $CO_2$ (%) | 9.4 | 10.0 | 8.6 | 8.4 | 7.2 |
| $H_2$ (%) | 6.53 | 5.9 | 8.2 | 6.2 | 4.0 |
| $CH_4$ (%) | 2.92 | 3.10 | 3.4 | 1.4 | 2.8 |
| $C_2H_6$ (%) | 0.4 | 0.1 | 0.01 | 0 | na |
| $C_2H_4$ (%) | 1.23 | 1.49 | 0.8 | 0.01 | na |
| $C_{3+}$ (%) | 0.14 | na | na | 0 | na |
| $N_2$ (%) | 67.5 | 67.2 | 71.9 | 75 | 76.7 |
| $H_2$/CO | 0.87 | 0.48 | 1.14 | 0.69 | 0.47 |
| Tar (gC/$Nm^3$) | ~4.3 | ~9.4 | ~0.99 | 1.94 | 32.8 |
| Total S (ppm) | 242 | 22 | 17 | 22.3 | na |
| $H_2S$ (ppm) | 104 | 34 | 12.7 | 7.5 | 10 |
| COS (ppm) | 19 | 3.9 | 1.2 | 14.5 | 18 |
| Methylmercaptane (ppm) | 0.8 | 0.4 | 0.7 | na | na |

na: not analyzed.

**Table 8:** Results for biomass gasification experiments.

| | **SP** | **WP** | **TWC** | **PC** | **MSS** |
|---|---|---|---|---|---|
| Fluidization velocity (m/s) | 0.41 | 0.43 | 0.43 | 0.24 | 0.17 |
| Residence time (s) | 1.22 | 1.17 | 1.17 | 2.11 | 2.95 |
| Cold gas efficiency (%) | 69 | 56 | 53 | 16 | 17.3 |
| Carbon conversion (%) | 82.2 | 69.7 | 59.1 | 25.9 | 26.7 |
| Gas yield ($Nm^3$/kg fuel) | 2.83 | 2.47 | 3.12 | 2.25 | 1.31 |
| Calorific value of the syngas per $Nm^3$ (MJ/$Nm^3$) | 4.40 | 4.25 | 3.50 | 2.33 | 2.51 |
| Calorific value of the syngas per kg gasified fuel (MJ/kg fuel) | 12.46 | 10.52 | 10.89 | 5.24 | 3.29 |

## CONCLUSIONS

Determination of the thermochemical conversion reactivity of six biomass feedstocks (straw pellet (SP), softwood pellet (WP), torrefied wood chips (TWC), pyrolysis char (PC), milled sunflower seed (MSS) and dried distillers' grains and solubles (DDGS)) under both pyrolysis and gasification conditions were studied. When the feedstock analysis results were compared, WP and TWC were the samples with relatively low ash content. On the other hand, in terms of agglomeration index (Si+P+K)/(Ca+Mg), SP seemed to be more prone to agglomeration during thermochemical conversion. The lowest ash fusion temperatures of SP supported its agglomeration tendency as well. Calculated activation energies and characterization studies of biomass feedstocks were indicated that, WP was more reactive to thermochemical conversion and less prone to agglomeration. Although MSS gave comparable activation energies with the WP, its high ash content and agglomeration index were the potential drawbacks in front of its utilization via thermochemical conversion. In the scope of gasification experiments, the highest cold gas efficiency and carbon conversion were obtained for the gasification of SP. On the other hand, SP had some drawbacks such as its high agglomeration tendency and low deformation temperature. It was observed that MSS produced the highest tar yield compared with the others This might be related to its lower bulk density and poor fluidization conditions inside the gasification reactor favoring fast pyrolysis conditions instead of gasification. WP was gasified with acceptable conversion values and efficiencies when compared with SP. When characterization results were evaluated together with the gasification studies, it was seen that WP would be the preferred fuel for an efficient and effective thermochemical conversion.

**Table 9:** The analysis of tar compounds for the gasification of different biomass samples

| **Tar Compound** | **Concentration (mg C/Nm$^3$)** | | | | |
|---|---|---|---|---|---|
| | **SP** | **WP** | **TWC** | **PC** | **MSS** |
| Benzene | 2061 | 4648 | 805 | 1344 | 21499 |
| Toluene | 539 | 1221 | 137 | - | 7091 |
| Xylene | 41 | 257 | 2 | - | 2172 |
| Ethylbenzene | 10 | 3 | 9 | - | 794 |
| Styrene (vinyl benzene) | 3 | - | - | - | - |
| Indene | 4 | 8 | 8 | - | - |
| Phenol | 14 | 13 | 1 | - | 113 |
| Napthalene | 1088 | 1795 | - | - | 490 |
| Methylnapthalene | - | 33 | 3 | - | - |
| Ethylnapthalene | - | 12 | - | - | - |
| Dimethylnapthalene | 24 | 6 | - | - | - |
| Acenapthalene | 74 | 251 | 7 | 122 | 136 |
| Fluorene | - | - | - | 181 | - |
| Diethylnapthalene | 7 | 9 | 5 | - | - |
| Antracene | 348 | 161 | 4 | - | 78 |
| Phenantrene | - | 761 | - | 205 | 47 |
| Pyrene | 132 | 253 | 5 | 70 | 45 |
| Total | ~4345 | ~9433 | ~986 | 1937 | 32780 |

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### Türkçe Öz ve Anahtar Kelimeler

# Farklı Biyokütle Hammaddelerinin Termokimyasal Dönüşüm Davranışı: Piroliz ve Gazlaştırma

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**Öz:** Bu çalışmada, tezgah ölçeğinde kabarcıklı akışkan yatak (BFB) gazlaştırıcı ve termogravimetrik analizör (TGA) kullanılarak gazlaştırma ve piroliz koşulları altında biyokütle yakıtlarının termokimyasal dönüşüm reaktivitesi tespit edilmiştir. Altı farklı biyokütle hammaddesi kullanılmıştır, bunlar hasır tanesi (SP), yumuşak kereste tanesi (WP), kurutulmuş odun kıymıkları (TWC), piroliz kömürü (PC), değirmenden geçmiş ayçiçeği tanesi (MSS) ve kurutulmuş damıtıcı tanesi ve çözünürleri (DDGS) olarak verilmiştir. Biyokütle hammeddelerinin TGA'sı dört farklı ısıtma hızında (2-15 °C/dakika) pirolitik koşullarda yürütülmüştür. Deneylerden elde edilen ham veriler örneklerin kinetik parametrelerini (A, $E_a$) hesaplamak için kullanılmıştır, burada Coats-Redfern ve Isoconversional Yöntem kullanılmıştır. TGA analizine göre piroliz kömürü 800 K'nin üzerindeki sıcaklıklarda bozunma sonucu kalan tek üründür, çünkü gazlaştırmadan önce buna ön piroliz uygulanmıştır. Türevli Termogravimetrik Analiz (DTG) profillerine göre, 450-650 K civarındaki iki pik ve iki omuz DDGS için gözlenirken piroliz kömürü için hiç bir pik elde edilmemiştir, bu da uçucu maddelerin veya selülozik bileşenlerin yokluğu anlamına gelmektedir. Yumuşak kereste ve kurutulmuş odun parçaları için elde edilen en yüksek uçuculuk giderme hızları ve uçuculuk giderme sıcaklıkları (temel olarak selülozun bozunması ile ilgilidir) diğer biyokütle hammaddeleri içinde en düşük kömür verimlerini oluşturmaktadır. WP'nin termokimyasal dönüşüme karşı daha reaktif olduğu ve kümeleşmeye karşı daha dayanıklı olduğu görülmüştür. Bunun dışında, MSS'nin yüksek kül yüzdesi ve kümelenme indisi termokimyasal dönüşüm yoluyla kullanılmasının önünde potansiyel engeller olarak durmaktadır. Bu hammaddelerin (DDGS dışında) havayla gazlaştırması sırasında, ürün olarak elde edilen sentez gazı temel gaz bileşimi, zift ve kükürtlü bileşikler cinsinden karakterize edilmiştir. En yüksek soğuk gaz etkinliği, karbon dönüşümü ve kalorifik değerler SP'nin gazlaştırılması için elde edilmiştir. Diğer taraftan, SP'nin yüksek kümelenme eğilimi ve düşük deformasyon sıcaklığından dolayı bazı dezavantajlar getirdiği bulunmuştur. Bütün hammaddeler içinde, MSS'nin gazlaştırma reaktifliğinin oldukça düşük olduğu bulunmuştur. MSS'nin gazlaştırma yerine pirolize uğradığı görülmektedir. WP ve TWC kabul edilebilir dönüşüm değerlerinde gazlaştırılmış ve etkinlikleri SP ile karşılaştırılmıştır. WP'nin termokimyasal dönüşümlerde tercih sebebi olduğu anlaşılmıştır.

**Anahtar kelimeler:** Termokimyasal dönüşüm; gazlaştırma; piroliz; sentez gazı; biyokütle.

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