Effect of Torrefaction Process Parameters on Biomass Feedstock Upgrading

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Abstract. *Biomass is a primary source of renewable carbon that can be utilized as a feedstock for biofuels or biochemicals production in order to achieve energy independence of energy importing countries. The low bulk density, high moisture content, degradation during the storage, and low energy density of raw lignocellulosic biomass are all significant challenges in supplying agricultural residues as a cellulosic feedstock. Torrefaction is a thermochemical process conducted in the temperature range between 200°C, and 300°C under an inert atmosphere which is currently being considered as a biomass pretreatment. Competitiveness and quality of biofuels and biochemicals may be significantly increased by incorporating torrefaction early in the production chain while further optimization of the process might enable its autothermal operation. In this study, torrefaction process parameters were investigated in order to improve biomass energy density, and reduce its moisture content. The biomass of choice (corn stover) at three levels of moisture content (30%, 45%, 50%) was torrefied at three different temperatures (200°C, 250°C, 300°C), and reaction times (10min, 20min, 30min). Solid, gaseous, and liquid products were analyzed and the mass/energy balance of the reaction was quantified. Overall increase in energy density, and decrease in mass and energy yield was observed as process temperature increased. Initial biomass moisture content affected energy density, mass, and energy yield especially at low process temperature, and high moisture feedstock.*

Keywords. Biomass, corn stover, torrefaction, pretreatment, physicochemical properties

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Introduction

Energy has always played an important role in life, survival, and development of mankind. Even though it is has been superseded by other, more potent fossil energy sources during the last 200 years, biomass was the major energy source since the beginning of civilization, and still plays important role in developing countries' economies. However, biomass recently has received renewed attention worldwide, mainly as a consequence of high and volatile oil prices, and global climate changes caused by increased fossil fuel consumption. Moreover, rapid economic growth in developing countries, high dependence of global and local transportation on fossil fuels, pollution, depletion of sources, endangered national security of energy importing countries has raised the awareness of the need for non-fossil, renewable energy sources (Demirbas, 2009; Klass, 1998; World Energy Council, 2009). Among renewable energy sources, such as wind, solar, geothermal, wave, tidal, and ocean thermal, biomass is the most prospective short term energy source with mature and readily applicable conversion technologies for production of most convenient transportation fuels - liquid fuels. Although in long term other forms of renewable energy may supersede biomass it will still remain as the only source of renewable carbon needed for chemicals and synthetic materials production.

According to Renewable Fuel Standard from Energy Independence and Security Act of 2007, minimum annual quantity of renewable fuel in U. S. transportation sector, should be increased from 9 billion in 2008 to 36 billion in 2022, where after 2016 most of renewable fuel must be, so called advanced biofuel derived from biomass instead from food crops (USA GPO, 2007). In order to sustain production demanded by RFS/2007 significant amounts of lignocellulosic biomass has to be collected from large areas, stored, and converted into biofuels.

However, the low bulk density, high moisture content, and low energy density of biomass feedstocks have a negative effect on the feasibility of long distance transportation. Moreover, in order to obtain such feedstock for continuous operation of biorefineries during the whole year, biomass has to be collected from large, and often distant areas, and hauled either to the local storage facilities or to the refiners, where it would be stored until conversion. Unfavorable physical properties of biomass dictate utilization of large storage facilities, which would further compromise economical use of biomass feedstock. In addition, storing such enormous amounts of wet biomass will further increase expenses through high rate of dry matter loss due to microbial activity and hazard of self-heating/combustion (Biomass Research Committee, 2007; Bridgeman et al., 2008; Arias et al., 2008, Lipinsky et al. 2002).

Thermochemical conversion technologies, such as pyrolysis, gasification, and hydrothermal processing, along with biomass co-firing in existing coal power plants, might have an important role in production of heat energy, advanced energy carriers, chemicals, solvents, and materials. However, all former technologies have strict demands regarding physical condition of biomass feedstock such as particle size and shape since these parameters influences size, throughput, and type of the reactor itself. Additionally the final products characteristics, yield, and distribution are also influenced by feedstock quality and composition (Klass, 1998). Moreover, because of biomass' recalcitrant nature it is difficult to grind it in an easy and cost effective way (Arias et al., 2008). Another issue that might influence feasible operation of biorefineries is heterogeneity of feedstock, considering not only different types of biomass, for example demolition wood, agricultural residues, and dedicated energy crops, or different plant species, but also same plant species grown in different areas (Yan et al., 2009; Bergman et al., 2005).

Torrefaction, sometimes also referred as a mild-pyrolysis, is a thermochemical process conducted in the temperature range between 200°C and 300°C under an inert atmosphere, and low heating rates. Torrefaction is currently being considered as a biomass feedstock

pretreatment particularly for thermal conversion systems. During torrefaction various permanent gases and condensables, with high oxygen content, will be formed mainly due to hemicellulose degradation. As a consequence the final solid product, so called torrefied biomass, will be composed mainly of cellulose and lignin and characterized by increased brittleness, hydrophobicity, microbial degradation resistance, and energy density. Thus torrefaction might have significant role in decreasing costs of transportation and storage of biomass in the large quantities needed to sustain biofuels production. In addition, torrefaction may have positive effect on pyrolysis, gasification, and co-firing units operation by lowering power consumption, and cost for biomass grinding, eliminating compounds responsible for high acidity of pyrolysis oil, and by increasing uniformity of biomass feedstock (Yan et al., 2009; Bergman et al., 2005; Prins et al., 2006; Bergman, 2005).

About 30 years ago, the process of torrefaction was first utilized, and operated commercially for the production of reducing agent for metallurgical industry, but since then it has received little attention. There have been several studies that investigated effects of torrefaction on biomass properties and composition of different fractions released during the process, but the majority of them focused on dry woody biomass which was finely ground before torrefaction. Analysis was conducted by utilizing either thermogravimetric analysis (TGA) or small scale reactors in experimental setup (Arias et al., 2008; Bergman et al., 2005; Prins et al, 2006; Couhert et al., 2009; Prins et al. 2006). Since agricultural residues will play an important role in production of advanced biofuels, but also have different properties from woody biomass, more research is needed to investigate the optimum torrefaction conditions for such feedstock. Potential for torrefaction of agricultural residues immediately after harvest without drying and before significant size reduction should be investigated in order to incorporate torrefaction early in the supply chain and utilize all its advantages. In this research we investigated the influence of torrefaction process parameters on the properties of corn stover biomass, characterized by different moisture contents. For this purpose we used Box Behnken design of experiments that allowed us to statistically model influence of different parameters on torrefied biomass properties. The results from this work will provide knowledge related to the influence of moisture on the process and torrefied biomass characteristics.

Objectives

In this research we investigated the influence of torrefaction reaction time, temperature, and moisture content of untreated corn stover feedstock on quantity and composition of three materials streams released from the torrefaction process: solids (torrefied corn stover), permanent gases and condensable volatiles. Quantitative and qualitative data from the analysis of solids, permanent gases and condensable volatiles were used to investigate mass and energy flows in the torrefaction process. Box Behnken design of experiments was utilized in this research in order to statistically model the torrefaction process in terms of mass and energy yields, and evaluate the significance of temperature, time, and untreated corn stover moisture content as predictors of response variables.

Materials and Methods

Materials

For the purpose of comprehensive characterization of torrefaction of corn stover feedstock the final torrefied solid product was recovered and analyzed while the volatiles released during the process as torrefaction gas were first separated into permanent gases and condensable volatiles fractions and then analyzed.

Corn stover samples, harvested during the fall 2009, were obtained from Department of Agricultural and Biosystems Engineering at Iowa State University, Ames, Iowa. This biomass is highly available agricultural residue in the Midwest and has been proposed as a feedstock for advanced biofuels production. After harvest samples were stored in the cooling chamber at 3-5°C to prevent feedstock degradation and minimize moisture loss.

Samples with 22%, and 41% moisture content were used directly from the field, while samples with 3% moisture content were obtained by drying corn stover with higher moisture content. In order to fit samples into the torrefaction reactor coarse grinding of corn stover was conducted. The samples were size reduced in a hammermill equipped with 25mm screen.

Torrefaction Chamber

Torrefaction experiments were conducted in the 2 L stainless steel fixed bed reactor, heated by three ceramic heaters in close contact with the reactor wall and separately controlled by PID controllers. This setup was used for coarse control of temperature, while fine temperature management was performed by means of preheated nitrogen gas. Figure 1 shows the position of four thermocouples inside the torrefaction reactor used for the temperature control. The nitrogen gas was also utilized for maintaining inert atmosphere during the experiments. For each experiment 4.5 L/min of nitrogen was purged through the reactor. Outlet tubing was also kept at an elevated temperature of about 200°C in order to prevent condensation of released volatiles.

Figure 1. Position of four thermocouples utilized for controlling the temperature inside the reactor

Gas Analysis

Volatiles and permanent gases released from the process were cooled immediately following release from the reactor by means of glass impingers submerged in an ice bath. This facilitated removing the majority of the condensables and water from the gas sample. Gas was then passed through desiccant columns before it was fed into a micro-gas chromatograph (Varian, Palo Alto, CA) equipped with a Molsieve 5A and Poraplot U columns.

Liquids Analysis

Liquid fractions collected in glass impingers were stored in the cooling chamber at 3-5°C until the analysis. Water content in condensed phase was analyzed according to Karl-Fischer method by a moisture titrator (KEM MKS-500, Kyoto Electronics, Tokyo, Japan) and ASTM E 203 – 08 standard method (ASTM Standards, 2008). Quantitative and qualitative analysis of organics present in condensed phase was conducted by a gas chromatogram equipped with Restek Stabilwax-DA column (Varian, Palo Alto, CA).

Ultimate Analysis

Ultimate analysis of the solid fraction was done with PerkinElmer (Waltham, MA) 2400 Series II CHNS/O Analyzer, according to ASTM D 5373 – 08 method. Raw biomass sample used as a reference was dried in an oven at 103°C for 24 h before ultimate analysis was done. Combustion was conducted at 925°C under helium atmosphere, while reduction was conducted at 650°C (ASTM Standards, 2008).

High Heating Value Determination

Higher heating value of raw, and torrefied biomass samples was computed using equation (1) developed by Sheng and Azevedo (Sheng and Azvedo, 2005).

HHV (MJ/kg) = -1.3675 + 0.3137 C + 0.7009 H + 0.0318 O   (1)

  C = Percentage of carbon in biomass as determined by ultimate analysis.

  H = Percentage of hydrogen in biomass as determined by ultimate analysis.

  O = Percentage of oxygen in biomass as determined by ultimate analysis.

Design of Experiments

The set of torrefaction experiments conducted to meet the objectives of this project were based on a Box-Behnken experimental design, which is a three level design based on the combination of a two level factorial design and incomplete block design. It is useful for statistical modeling and optimization of a response variable of interest, which is a function of three of more independent variables. Moreover, Box-Behnken designs allow estimating coefficients in a second degree polynomial regression and modeling of a quadratic response surface. The response surface can be further used for process optimization, identification of maximum or minimum responses, and significance of each involved factor, or their combination. Furthermore, response surfaces can be used for calculating responses not only at experimentally investigated points, but also at any point on the surface (Box and Behnken, 1960; Calborn and Matuana, 2006; Muthukumar et al., 2003). In this work a three factor-three level Box-Behnken design, with 5 replicates at the center point, and 17 runs in total (table 1). JMP statistical package from SAS was used for the statistical analysis of experimental data.

Table 1. Box Behnken experimental design matrix generated by JMP

No.	Pattern	Moisture	Temperature	Time
1	− −0	3	200	20
2	− 0−	3	250	10
3	− 0 +	3	250	30
4	− + 0	3	300	20
5	0 − −	22	200	10
6	0 − +	22	200	30
7	0 0 0	22	250	20
8	0 0 0	22	250	20
9	0 0 0	22	250	20
10	0 0 0	22	250	20
11	0 0 0	22	250	20
12	0 + −	22	300	10
13	0 + +	22	300	30
14	+ − 0	41	200	20
15	+ 0 −	41	250	10
16	+ 0 +	41	250	30
17	+ + 0	41	300	20

Results and Discussion

Process time and temperature were defined such that the torrefaction process temperature was the average of temperatures measured by four thermocouples within the torrefaction reactor during the experiment. The torrefaction start time was measured from the point when the temperature first achieved temperature proposed in the design. Figure 2 depicts an average temperature profile for one of the experiments at 250°C.
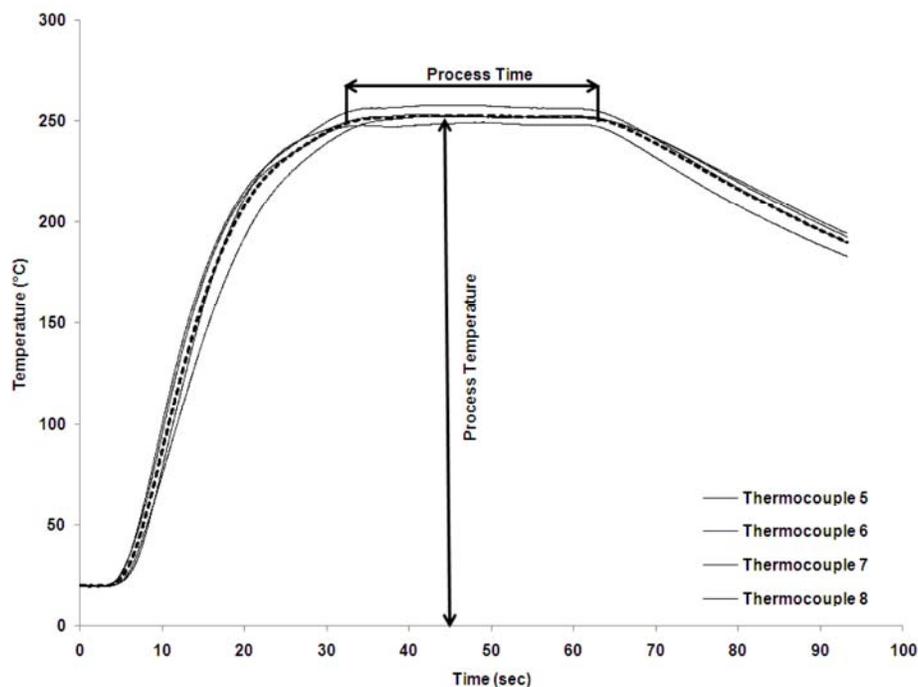
Figure 2. Temperature profiles for four thermocouples and average temperature profile used to determine process temperature and time

Mass balances for the torrefaction process were computed based on the results from the solid, liquid, and gas analysis. Mass balances for torrefaction experiments conducted at low temperatures proved accurate regardless of moisture content, and time. However, at 300°C errors in mass balance occurred mainly due to lower yield of solid, torrefied material that can be weight directly and an increased yield of volatiles that will condense throughout the exhaust system and are hard to recover. Additionally, a high amount of aerosols formed at this temperature would require either electrostatic precipitators or filters to accurately account for their mass.

Table 2. Total mass balance for torrefaction experiments

Sample ID	Raw Biomass Moisture Content [%]	Process Parameters Temp.-Time [°C/min]	Torrefied Biomass Yield [%]	Condensables Yield [%]	Permanent Gases Yield [%]
3-200-20	3.2	200-20	97.1	0.02	0.4
3-250-10	3.2	250-10	86.6	1.79	1.1
3-250-30	3.2	250-30	84.4	4.07	1.4
3-300-20	3.2	300-20	57.4	13.30	2.7
22-200-10	22.1	200-10	98.1	0.39	0.5
22-200-30	22.1	200-30	98.4	0.40	0.6
22-250-20	22.1	250-20	86.2	4.32	1.3
22-250-20	22.1	250-20	85.3	4.37	1.3
22-250-20	22.1	250-20	83.4	4.39	1.5
22-250-20	22.1	250-20	83.5	4.26	1.4
22-250-20	22.1	250-20	83.4	4.09	1.4
22-300-10	22.1	300-10	58.0	11.52	2.0
22-300-30	22.1	300-30	53.9	18.39	3.3
41-200-20	41.0	200-20	91.2	0.66	0.6
41-250-10	41.0	250-10	80.0	3.79	1.2
41-250-30	41.0	250-30	78.7	6.11	1.3
41-300-20	41.0	300-20	56.3	18.59	2.9

There is an overall trend of decrease in yield of solids and increase in yield of permanent gases and condensable products as both temperature and reaction time increase (Table 2). Loss in solids yield is much more pronounced between 250°C and 300°C, than between 200°C and 250°C, regardless of moisture content of samples. This is likely due to higher reactivity or more extensive devolatilization and decarbonization of hemicellulose fraction above 250°C. Along with degradation of hemicellulose, initial reactions of cellulose decomposition might occur in this temperature regime, as proposed by other researchers (Koukious, 1982) . The same trend is observed for the yield of condensables, and permanent gases. However, at 300°C, regardless of moisture content in raw feedstock, yield of condensables is much higher than yield of permanent gases, which might be evidence of more intensive decomposition of not only hemicellulose, but also other polymer fractions. This would support the production of heavier compounds responsible for tar formation observed in condensed phase during the experiments. There is an evident influence of moisture content on loss in mass yield at 250°C, and especially at 200°C, where mass loss of samples with 45% moisture content is 3 times higher than that of samples with 3%, and 22% moisture content in raw biomass (Figure 3).
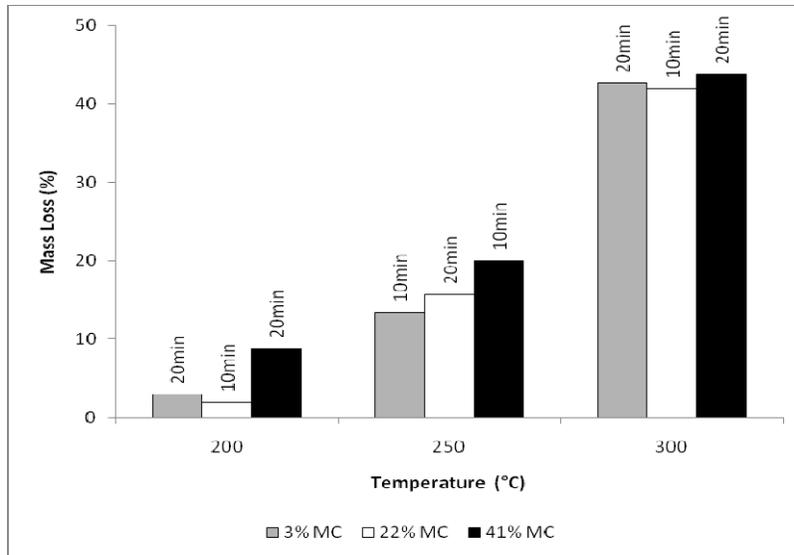
Figure 3. The effect of untreated biomass moisture content on mass loss of torrefeied samples.

This interaction of mass loss and moisture content of the feedstock has not previously been reported in scientific journals and is of high importance for designing a commercial scale torrefaction system. A possible reason for this might be the expansion of water vapor inside the plant polymer matrix during the ramping stage of biomass heating. This expansion will loosen the material and make it less resistive to heat transfer. Since water has higher heat conduction coefficient than both air and nitrogen it will additionally enhance heat transfer in samples with high moisture content. It is proposed in the literature (Prins, 2005) that at heating rates lower than 50°C/min the parameter that restricts torrefaction reaction is reaction kinetics rather than heat transfer through the particle. In this case this might not be true since particle size in these experiments were relatively large and representative of a real agricultural residue feedstock.

Moreover, since a packed bed reactor is used in this project a higher specific heat of water vapor than nitrogen gas might increase the amount of heat delivered to the zones closer to the top of reactor and enhance degradation of biomass. Another cause might be probability of close contact between released acids with biomass structural polymers, especially hemicellulose, as a result of increased specific area caused by expansion of water vapor. According to literature (Huber et al., 2006), short chain organic acids may act as a catalyst, thus promoting mainly hemicellulose degradation at this reaction conditions, but also to a lesser extent, degradation of other polymers. As a consequence of a more aggressive environment during the processing of high moisture biomass milder conditions (temperature/time) might be used to achieve the same effect as in the case of lower moisture content biomass torrefied at more extreme conditions. Nevertheless, there is almost no difference between mass loss of different samples at the most extreme time/temperature combinations regardless of sample moisture content. This might be due to accelerated thermal degradation of cellulose and lignin, in this temperature zone, after total amount of hemicellulose is decomposed at lower temperatures, which would ultimately eliminate any initial difference between the samples.

Experimentally obtained mass loss data were analyzed using JMP statistical software, and fitted into response surface quadratic model (equation 2), since this is one of the values of interest in our current experiments.

Predicted Mass Loss = 95.68 – 0.501*Time – 1.0396*Temperature + 0.2491*Moisture + 0.0022*Time*Temperature – 0.0011*Time*Moisture – 0.0012*Temperature*Moisture + 0.00167*(Time)^2 + 0.00284*(Temperature)^2 + 0.0044*(Moisture)^2 (2)

The summary of fit and analysis of variance are given in table 3 and table 4 respectively. As can be seen from table 3 the mass loss response surface model is in good agreement with actual data obtained in experiments. Moreover, table 4 shows that the model is significant which is justified by small p-value.

Table 3. Summary statistics for the mass loss response surface model with three predictors: moisture, temperature and time

RSquare	0.993442
RSquare Adj	0.98501
Root Mean Square Error	1.807702

Table 4. ANOVA for the mass loss response surface model with three predictors: moisture, temperature and time

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	9	3465.1031	385.011	117.8203
Error	7	22.8745	3.268	Prob > F
C. Total	16	3487.9776		<.0001*

According to the model significant parameters are temperature, moisture, and temperature squared. The strength or effect of two significant process parameters on the dry matter mass loss is better revealed by surface and contour plots in the figure 4 and figure 5, respectively. Effect of moisture content of raw biomass on dry matter loss is depicted on both plots by more pronounced curvature in the temperature region below approximately 260°C, and moisture content above about 20%.
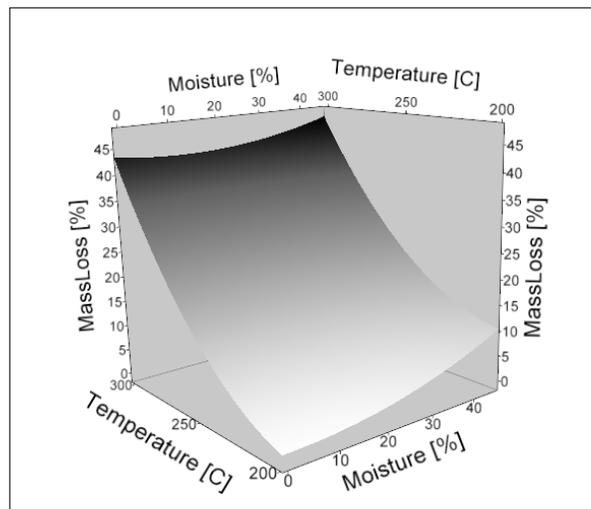
Figure 4. Surface plot of the effect of temperature and mosture content of raw biomass on predicted mass loss (time = 20min)
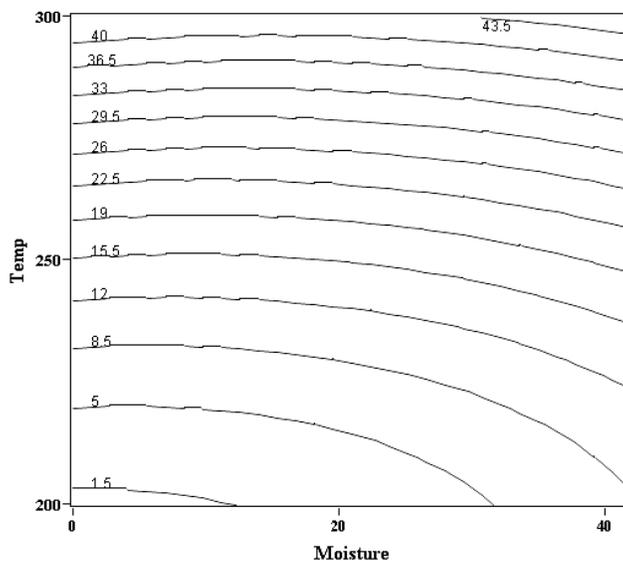
Figure 5. Contour plot of the effect of temperature, and moisture on dry matter loss (time = 20min)

As revealed by figure 6, water represents largest portion of condensables released during the torrefaction process, followed by acetic acid, and furfural, methanol, and hydroxyacetone in much smaller quantities. The water represented in figure 6 is only reaction water and does not include water associated with the initial moisture content of the biomass. Water is formed in the process of polymer dehydratation through the release of hydroxyl groups while acetic acid and methanol are formed from acetoxy and methoxy groups attached to hemicellulose sugar monomers and lignin. Other compounds are generated at high temperature by thermal decomposition of plant polymer monomers. As can be seen in the figure 6, the amount of condensables released during torrefaction of biomass samples with initial moisture content of 22%, and 41% are not significantly different. However, they are two times higher than in the case of torrefaction of samples with 3% initial moisture content. This is mainly due to acetic acid which might be explained by positive influence of water on polymer decomposition reactions and acceleration of such reactions.
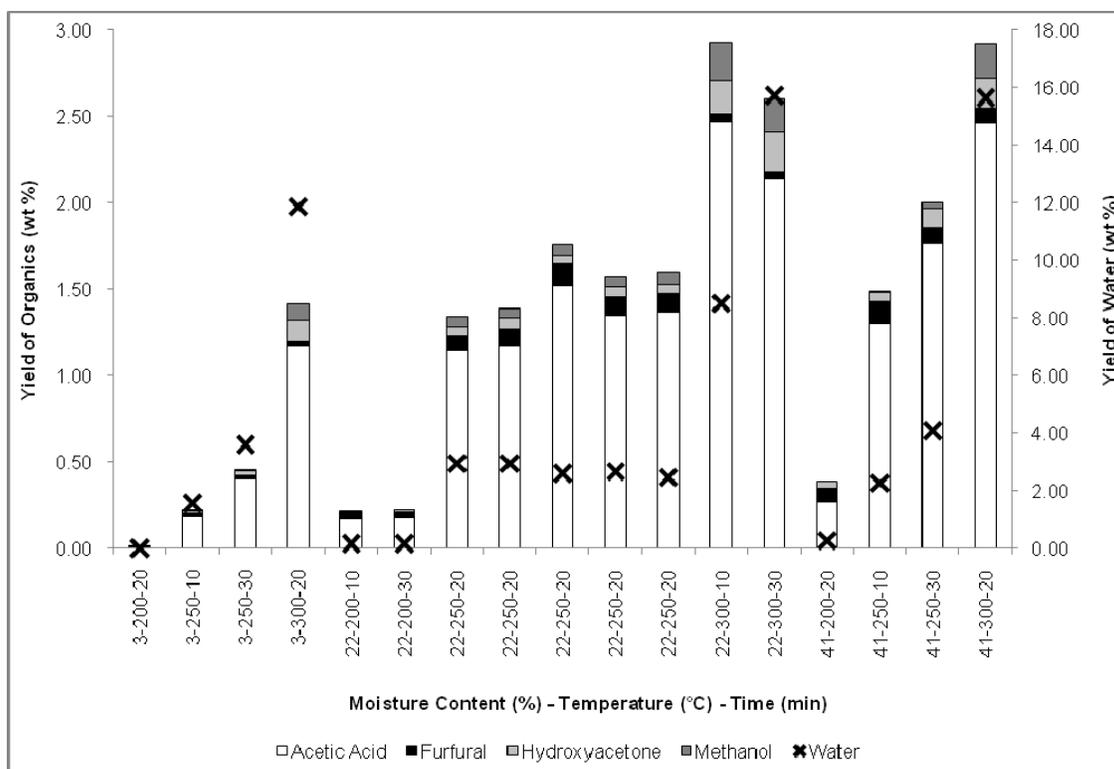
Figure 6. Composition of condensable volatiles released during torrefaction

Figure 7 shows composition of permanent gas phase released during the torrefacion of biomass with different initial moisture content and at various combinations of process parameters. In the figure 7 only carbon monoxide and carbon dioxide are shown, since they are the main gas components even though traces of methane, and hydrogen are present at high reaction temperature. As can be seen in the figure 7, ratio of carbon monoxide and carbon dioxide increases both with temperature and time. This is different from influence of time on mass yield which does not have a significant effect. Departure of gas composition from this trend for sample 22-300-10, might be due to problems with temperature control during this experiment. Nevertheless, composition of permanent gas phase is not affected significantly by moisture content in raw feedstock. Production of carbon dioxide during the process might be explained by decarboxilation of acid groups attached to hemicellulose, while carbon monoxide may be produced in reaction of carbon dioxide, and steam with char at high temperatures (White and Dietenberger, 2001).

Torrefaction increases the amount of atomic carbon while decreases the amount of atomic hydrogen and oxygen as shown in table 5. A consequence is the chemical composition change is the decrease in the atomic O/C and H/C ratio of torrefied biomass in comparison to raw biomass. This is due to release of volatiles rich in hydrogen and oxygen, such as water and carbon dioxide. Decrease in O/C, regardless of moisture content in raw biomass, can be up to about 7%, 15%, and 45% at 200°C, 250°C, and 300°C respectively. This change in chemical composition of biomass will improve its quality as an energy source through increase in energy density since more oxygen than carbon is lost in form of volatiles.
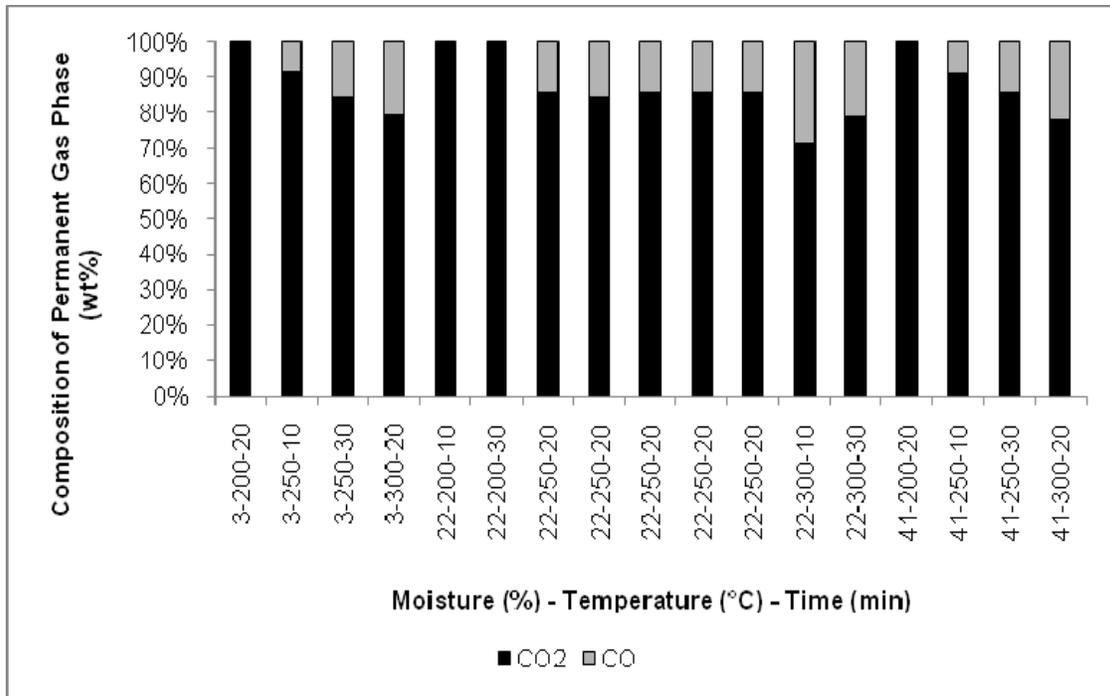
Figure 7. Change in permanent gas composition with process parameters, and raw biomass moisture content

Table 5. Ultimate analysis and computed energy density of torrefied samples

Sample	C [wt%]	H [wt%]	N [wt%]	O [wt%]	HHV [MJ/kg]
3-200-20	45.8	5.5	0.5	48.2	18.4
3-250-10	47.7	5.3	0.6	46.4	18.8
3-250-30	49.1	5.4	0.6	45.0	19.2
3-300-20	58.7	4.7	0.7	35.8	21.5
22-200-10	45.7	5.7	0.7	47.9	18.5
22-200-30	45.8	5.5	0.6	48.1	18.4
22-250-20	49.1	5.4	0.7	44.8	19.2
22-250-20	48.3	5.5	0.6	45.6	19.1
22-250-20	49.2	5.4	0.7	44.7	19.3
22-250-20	49.4	5.4	0.6	44.5	19.3
22-250-20	48.7	5.4	0.6	45.3	19.1
22-300-10	56.6	4.9	0.9	37.6	21.0
22-300-30	59.0	4.7	1.0	35.4	21.6
41-200-20	45.6	5.4	1.0	48.0	18.2
41-250-10	48.2	5.3	0.9	45.6	18.9
41-250-30	48.8	5.2	0.9	45.1	19.0
41-300-20	55.8	4.8	1.1	38.2	20.8
Raw	44.2	5.8	0.5	49.5	18.2

Another important characteristic of torrefied corn stover is increase in energy density when compared to raw biomass. This is the result of a decrease in mass of torrefied samples through the release of compounds rich in oxygen and hydrogen. It can be seen from the figure 8 that temperature has highest impact on energy density of torrefied biomass, while the effect of time, and moisture is much less expressed.
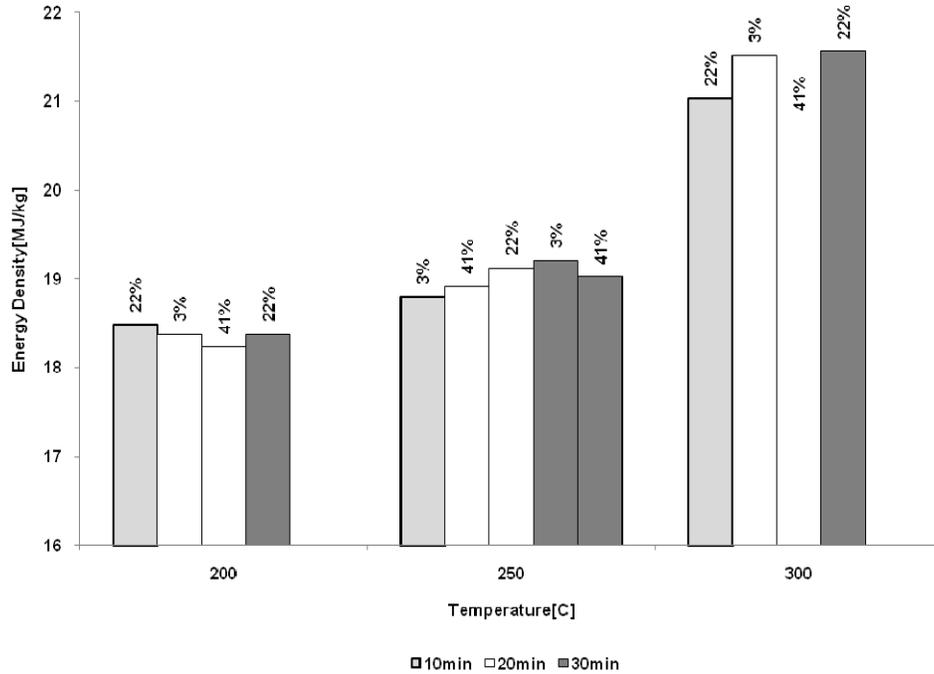
Figure 8. Effect of process parameters and raw biomass moisture content on energy density of torrefied material

Energy yield per dry raw biomass indicates the total energy preserved in the torrefied biomass. It was computed from mass yield and higher heating values using equation 3and expressed as a percentage of energy content of untreated dry biomass.

$$E_{yield} (\%) = (m_{torrefied} / m_{initial})_{dry\ basis} \times E_{torrefied} / E_{initial\text{-}dry\ basis} \qquad (3)$$

> $m_{torrefied}$ = mass of biomass feedstock measured after torrefaction expressed on dry basis
>
> $m_{initial}$ = mass of untreated (raw) biomass feedstock measured before torrefaction expressed on dry basis
>
> $E_{torrefied}$ = specific energy content of biomass feedstock after torrefaction expressed on dry basis
>
> $E_{initial\text{-}dry\ basis}$ = specific energy content of biomass feedstock before torrefaction expressed on dry basis

Energy yields computed using given equation are shown in the figure 9.
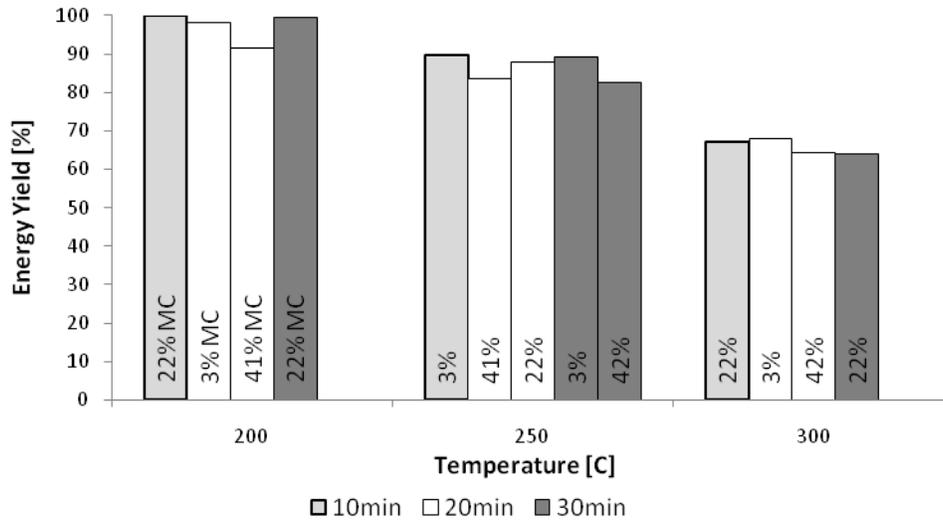
Figure 9. Effect of process parameters and initial moisture content of untreated biomass on energy yield

These values were fitted into response surface model represented by equation 4, in order to analyze the effect of process parameters on energy yield.

Predicted Energy Yield = 10.0379 - 0.0144*Moisture + 0.9278*Temperature + 0.498*Time + 0.0007612*Moisture*Temperature – 0.000658*Moisture*Time – 0.00145*Time*Time – 0.00721*Moisture^2 – 0.002461*Temperature^2 – 0.004525*Time^2 (4)

As shown in table 6 and table 7, fitted model is in good correlation with actual data which is justified by relatively high R values, while according to small p-value in ANOVA table our model is significant.

Table 6. Summary statistics for the energy yield response surface model with three predictors: moisture, temperature and time

RSquare	0.989985
RSquare Adj	0.977108
Root Mean Square Error	1.804479

Table 7 – ANOVA for the for the energy yield response surface model with three predictors: moisture, temperature and time

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	9	2253.0694	250.341	76.8827
Error	7	22.7930	3.256	Prob > F
C. Total	16	2275.8624		<.0001*

In this model the significant parameters are temperature, temperature squared, moisture, and moisture squared.

As revealed in figure 10 and 11, biomass torrefied at lower temperatures has the highest energy yield, which is expected since this parameter is strongly dependant on mass yield which is

significantly affected by process temperature. Moisture has much weaker influence on energy yield than temperature as seen in the figure 10 and figure 11.
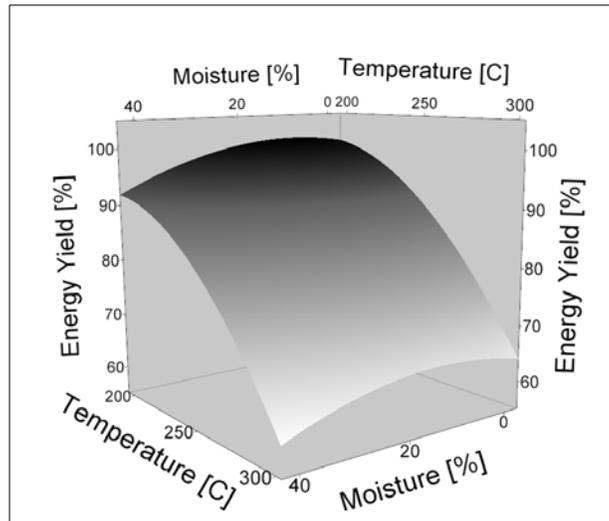
Figure 10. Surface plot of the effect of temperature and mosture content of raw biomass on predicted energy yield (time = 20min)
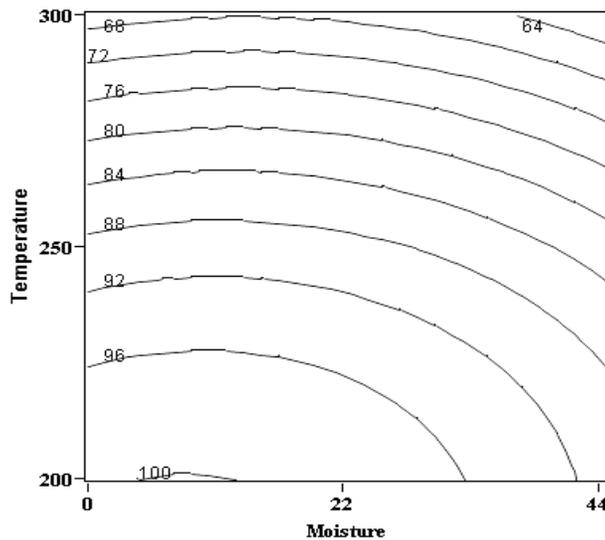
Figure 11. Contour plot of effect of temperature, and moisture on energy yield (time = 20min)

However, initial moisture content induced up to 10% more energy loss at temperatures below 220°C and raw biomass moisture content higher than 20%. This is correlated with mass loss and justified by the similar contour plot curvature in the figure 4 and 5. Moreover, as displayed in figure 11, moisture has a stronger influence on energy yield than on mass loss, even at 300°C. This might be due to the loosening effect of water on fibrous matrix, its role in polymer hydrolysis and formation of organic acids that promotes more extensive cellulose and lignin degradation through high energy volatile compounds, such as tar.

Conclusion

Corn stover undergoes different changes in chemical composition, mass, and energy content during the torrefaction process. As expected these changes were more extensive at high temperatures and characterized by mass loss up to 45% as well as a decrease in O/C ratio from 1.11 to 0.6 and an increase in energy density of about 19%. However, high mass losses offset gains in energy density and significantly reduced overall energy yield. Moisture content had a significant effect on energy density, mass and energy yield, and generally induced reduction in each of these parameters. Moreover, the effect of moisture is more pronounced at lower temperatures, where if moisture content in raw biomass is increased from 22% to 44%, energy yield could be reduced to about 10%.

Nevertheless, there is a raw biomass moisture content window between 3% and approximately 20% that can allow for the use of corn stover feedstock directly from the field without any negative effect on energy yield. Furthermore, results from our experiments suggest that corn stover with 10% moisture content might have higher energy yield then dry biomass regardless of torrefaction temperature.

Further research should be done on torrefied biomass at proposed process parameters in order to determine the alteration of fiber composition and quantity. Additionally, physical properties, such as grindability and behavior during pelletization need to be more thoroughly quantified. Moreover, results obtained in these experiments should be included in response surface quadratic models and used to optimize the process according to desired characteristics of final product. In order to assess potential for autothermal operation, it is necessary to investigate combustibility of volatiles released at different combinations of process parameters and raw biomass moisture contents.

Despite inevitable losses in energy yield during the process, additional research in the future might justify use of torrefaction as a biomass pretreatment, or upgrading step, by obtaining data that will prove savings in torrefied biomass particle size reduction, improvement in storage stability, hydrophobicity, and properties important for other thermochemical processes, such as pyrolysis, gasification, co-cofiring.

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