COMPARISON OF BIOLOGICAL AND THERMAL (PYROLYSIS) PATHWAYS FOR CONVERSION OF LIGNOCELLULOSE TO BIOFUELS

A Dissertation

by

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ABSTRACT

Because of the limited supply of imported crude oil and environmental degradation, renewable energy is becoming commercially feasible and environmentally desirable. In this research, biological and thermal (pyrolysis) conversion pathways for biofuel production from lignocellulosic feedstocks were compared. For biological conversions of sorghum, ethanol yield was improved using M81-E variety (0.072 g/g juice) over Umbrella (0.065 g/g juice) for first-generation biomass (sorghum juice), and 0.042 g/g sorghum was obtained from the cellulosic portion of second-generation biomass. When ultrasonication was combined with hot water pretreatment, yields increased by 15% and 7% for cellulose to glucose, and hemicellulose to pentose, respectively. Ethanol yield was 10% higher when this pretreatment was combined with Accellerase 1500+XC for saccharification. Biological conversion yielded 1,600−2,300 L ethanol/ha for first-generation biomass, and 4,300−4,500 L ethanol/ha from lignocellulosic biomass.

For thermal (pyrolysis) conversion of lignocellulosic switchgrass at 600 ^{o}C, product yield was 37% bio-oil, 26% syngas, and 25% bio-char. At 400 ^{o}C, product yield was 22% bio-oil, 8% syngas, and 56% bio-char. Bio-oil from pyrolysis was highly oxygenated (37 wt%). It required chemical transformation to increase its volatility and thermal stability, and to reduce its viscosity by removing objectionable oxygen, so the product could be used as transportation fuel (gasoline). As a consequence of upgrading bio-oil by catalytic hydrogenation, bio-oil oxygen decreased from 37−2 wt%, carbon increased from 50−83 wt%, hydrogen increased from 9−15 wt% and heating value

increased from 36−46 MJ/kg, resulting in a fuel that was comparable to gasoline. The upgraded product passed the thermal stability test when kept under an oxygen-rich environment. The upgraded product consisted of 14.8% parrafins, 21.7% iso-parrafins, 3% napthene, 42.6% aromatics, 4.7% olefin, 4.7% DMF, 8% alcohol, and 0.6% ketone on a mass basis.

Comparing the two pathways, biological conversion had 11 wt% ethanol yield from sorghum, and thermal conversion had 13 wt% gasoline yield from switchgrass. For process efficiency, thermal conversion had 35% energy loss versus 45% energy loss for biological conversions. For the biological pathway, ethanol cost was $2.5/gallon ($4/gallon, gasoline equivalent), whereas for the thermal pathway, switchgrass gasoline cost was $3.7/gallon, both with 15% before tax profit.

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1. GENERAL INTRODUCTION

The main motives for using biomass as a renewable energy source for automotive fuel are attempts to (1) reduce the use of non-renewable fossil energy, (2) improve energy security (US DOE, 2002), and (3) improve the environment (Demirbas, 2001). Renewable energy is becoming commercially feasible and environmentally desirable in the United States (McLaughlin et al., 2002), because of the high cost of imported crude oil and increased oil prices (Wiedenfield, 1984), environmental degradation (Lynd et al., 1991), and future agricultural land retirement programs (Somerville et al., 2010) that will result in increased production of biomass for conversion to clean-burning liquid fuels. Advances in the technology required for commercial production of renewable transportation biofuels have greatly accelerated as fossil fuel sources continue to deplete (Gray et al., 2006).

Feedstocks used for biofuel include: (1) fast-growing trees or switchgrass; (2) agricultural residues and by-products such as straw, sugarcane fiber, and rice hulls; and (3) residues from forestry, construction, and other wood processing industries (Crocker, 2006; Medlock, 2001). These biomass sources are considered as clean energy (Speight, 2011). Biomass contains negligible amounts of nitrogen, sulfur, and ash, which results in a lower emission of SO_2, NO_x, and soot than conventional fossil fuels (Zhang et al., 2006; Borjesso, 1996). In addition, CO_2 released from biomass is incorporated into plants by photosynthesis quantitatively (Speight, 2011). The Climate Solutions Report estimated that 512 million dry tons of biomass residues are available in the United States for use in energy production (Mazza, 2001). Fuels derived from biomass are renewable

and are sufficiently similar to fossil fuels to provide direct replacement (Mielenz, 2001). Importantly, no net carbon dioxide would be added to the environment if biomass energy replaced fossil fuels (Farrell et al., 2006). Therefore, the need for biofuel production from biomass becomes significantly important.

1.1 Dissertation organization

This dissertation consists of six chapters. Chapter I is a general introduction that consists of literature review of technical pathways to produce biofuel from biomass, pretreatment and hydrolysis in lignocellulose breakdown, pyrolysis oil upgrade technologies, problems with the current technology, hypotheses, goals and objectives developed based on limitations discussed, and finally, the approaches of biomass conversion to biofuel used in this research. Chapter II presents a comparison study of biological conversion of first-generation feedstock (different varieties of sweet sorghum juice) and second-generation feedstock (lignocellulosic sweet sorghum) to bio-ethanol. Chapter III reports a study of thermal conversion of lignocellulosic biomass (switchgrass) to bio-oil, synthesis gas, and bio-char. Chapter IV presents the design, development, and test results of a catalytic upgrading process system that uses a novel pathway to upgrade bio-oil to transportation fuel (gasoline). Chapter V compares biological and thermal conversion pathways. Chapter VI reports overall conclusions for this research and recommendations for future work.

1.2 Literature review

1.2.1 Technical pathways for production of bio-energy from biomass

Biomass can be converted to biofuels suitable to substitute for transportation fossil fuels, heating, and electricity generation (Metzger, 2006). Such conversions are accomplished through various distinct processes, which include biological, chemical, thermal, and combinations of these (biochemical) to produce gaseous, liquid, and solid biofuels. These fuels (Table 1.1) have high energy contents, are easily transportable and therefore are suitable for use as commercial fuels. Table 1.1 presents the technologies and conversion processes that can be used to convert biomass to bio-energy or biofuel.

Table 1.1
Bio-energy production technologies from biomass.

Technology	Conversion process type	Major biomass Feedstock	Energy or fuel produced
Direct combustion	Thermochemical	wood, agricultural waste municipal solid waste	heat, steam electricity
Gasification	Thermochemical	wood, agricultural waste municipal solid waste	CO, H_2, CO_2
Pyrolysis	Thermochemical	wood, agricultural waste municipal solid waste	bio-oil, char syngas
Anaerobic digestion	Biochemical	animal manure agricultural waste landfills, wastewater	methane, CO_2
Ethanol production	Biochemical	sugar or starch crops wood waste, pulp sludge grass straw	Ethanol
Biodiesel production	Chemical	rapeseed, soy beans waste vegetable oil animal fats	Biodiesel

Source: http://www.oregon.gov/ENERGY/RENEW/Biomass/BiomassHome.shtml#chart

Combustion, gasification, and pyrolysis are thermal conversion processes by which bio-energy is obtained from biomass. Pyrolysis, rapid decomposition of organic materials in the absence of oxygen, is a promising thermal approach that was studied in this research. Pyrolysis can be used to convert biomass into energy in the forms of liquid bio-oil, solid bio-char, and syngas composed of H_2, CO, CO_2 and low-molecular-weight hydrocarbon gases (Yang et al., 2004; Rao and Sharma, 1998; Boateng et al., 2006). Compared to other methods of energy conversion, advantages of pyrolysis include: (1) drastic reduction of solid residue volume (Inguanzo et al., 2002); (2) carbonaceous matrices containing heavy metals are relatively resistant to natural lixiviation (Caballero et al., 2001; Bridgewater and Peacocke, 2000); (3) high-energy-value oil and gas products that can be potential fuels; and (4) low-temperature processing compared to incineration, which limits gas pollutants because the absence of air lowers dioxins (Liu et al., 2011). Pyrolysis is conducted at temperatures between 400 and 600 ^{o}C (Mullen et al., 2010). Bio-oil from pyrolysis can be upgraded to transportation fuel (Yang et al., 2010), and syngas from pyrolysis can be used to generate power; the H_2 can be used for hydrogenation in the upgrading process of bio-oil, and bio-char can be used as fertilizer (Boateng, 2006).

Biochemical conversion of biomass includes: (1) fermentation of sugars (first generation), and lignocellulose (second generation) to alcohol for liquid fuel and, (2) anaerobic digestion of biomass for bio-gas production (Table 1.1). In this research, both first- and second-generation feedstocks were studied for bio-ethanol production. The three major processes of bio-ethanol production from biomass are direct fermentation of

sugar feedstock (sugarcane) (Lorber et al., 1984; Wingren, 2003), enzymatic conversion of starchy feedstock (grains and corn) (Laluce and Mattoon, 1984; Potter et al., 1995; Akpan et al., 2005), and acid/enzymatic saccharification of lignocellulosic feedstock (fibrous plant material) (Badger, 2002; Hammerschlag, 2006; Lynd, 1996). Bio-ethanol produced from biomass has been used in internal combustion engines in Brazil and as a blend with gasoline in the United State (Tyson et al., 1993).

1.2.2 Pretreatment and hydrolysis in lignocellulose breakdown

Lignocellulosic biomass is composed of lignin, hemicellulose and cellulose (Figure 1.1). In general, lignin contains three aromatic alcohols (coniferyl, sinapyl, and pcoumaryl) and is covalently linked to hemicelluloses (Hons et al., 1986). Hemicelluloses are polymers of pentoses (xylose and arabinose), hexoses (mostly mannose), and some sugar acids. Cellulose is a homogenous polymer of glucose (Aden and Foust, 2003).

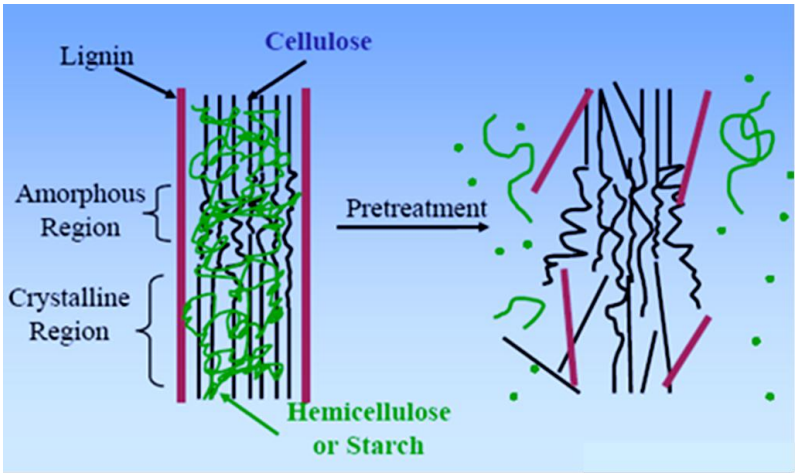


Fig. 1.1. Lignocellulosic biomass is composed of lignin, hemicellulose, and cellulose (Mosier et al., 2005; Hsu et al., 1980).

Table 1.2 summarizes various pretreatment process specifications and the advantages and disadvantages of each.

Table 1.2
Pretreatment summary for biological conversions.

Pretreatment	Process	Benefits	Problems	References
Mechanical	grinding, milling, chipping	reduce cellulose crystallinity	Expensive	Takacs et al., 2000 Sun & Cheng, 2002
Steam explosion	120–240 C 0.69–4.83 MPa	high glucose yield, cost effective	xylan degrade inhibitor form	Li et al., 2007 Tucker et al., 2003
Liquid hot water	150–200 ^{0}C slurry biomass	no/low inhibitor, low solubilized cell concentration	cellulose degradation based on condition	Mosier et al., 2005 Laser et al., 2002
Acid (dilute or strong)	H_2SO_4, HCL, H_2PO_4, HNO_3	high glucose & pentose yield	corrosive, toxic, expensive, inhibitors form	Taherzadeh & Karimi, 2007 Schell et al., 2003 Goshadrou et al., 2011
Alkali and Lime	NaOH, KOH, lime: $Ca(OH)_2$, CaO	surface area increase, DP decrease lime: cheap, easy recovery, high cellulose recovery	high xylan loss, alkaline recovery	Mosier et al., 2005 Xu et al., 2010 Karr & Holtzapple, 2000 Chang et al., 2001
Ammonia fiber explosion (AFEX)	liquid NH_3 at high *T* and *P* sudden *P* reduce	surface area increase, low inhibitor, high glucan & xylan conversion	ammonia recovery, less effective high-lignin biomass	Gollapalli et al., 2002 Murnen et al., 2007 Isci et al., 2008
Ozonolysis	35 mg/L @ 25^{o}C	effective delignification, no inhibitor, mild *T* & *P*	large ozone, expensive	Goel et al., 2003 Roncero et al., 2003
Biological	brown & white rot fungi	environment friendly, low energy input	lengthy process cellulose loss	Okano et al., 2005 Lee et al., 2007 Singh et al., 2008
My pretreatment	Ultrasonic+ LHW	no expensive chemicals, not lengthy – 1 h	high energy, depending on condition	Goshadrou et al., 2011 Imam & Capareda, 2012

Bioconversion of lignocellulosic materials to useful, higher value products usually requires multi-step processes that include: (i) pretreatment to remove some of the lignin wall, disrupt the crystalline structure of the cellulose and pre-hydrolyze the hemicellulose to release hexoses and pentoses by mechanical treatment (size reduction through milling and extrusion processes) (Corredor, 2008); chemical disaggregation (using dilute or concentrated acid, hot water, or organic solvent treatment, steam or ammonia fiber explosion) (Zhan et al., 2006); biological (microbial and enzyme) degradation; or combinations of these methods (Grethlein, 1984; Grethlein, 1991); (ii) enzymatic hydrolysis of the polymers to produce readily metabolizable molecules – hexose or pentose sugars (Sun and Cheng, 2002); and (iii) bio-utilization of these molecules to support microbial growth to produce biofuel (Corredor, 2008). Because enzymatic hydrolysis favors release of sugars during hydrolysis, and does not corrode the reactor, recently, this approach has been favored over acid hydrolysis (Dien et al., 2006; Saballos et al., 2008).

Enzymes for degrading lignocellulose require a three-enzyme system: (1) endoglucanase cleaves internal β (1-4) glucosylic bonds on the straight chains of the cellulose molecule (Delgenes et al., 1996), (2) exoglucanase breaks the ends of cellulose chains to form oligosaccharides, and (3) β-glucosidases hydrolyze soluble oligosaccharides to glucose for the cellulosic structure (Adhi et al., 1989). The cellulose structure contains β (1-4) bonds in straight chains that are attached to other straight chains by hydrogen bonds that are difficult to break, and make hydrolysis more difficult. The lignocellulose cell walls containing intermeshed carbohydrate and lignin polymers

that require high input energy to disaggregate, and make the structured available to the enzymes to perform the hydrolysis.

Hydrolysis of cellulose and hemicellulose can be performed enzymatically, or chemically by dilute sulfuric acid. Table 1.3 lists some of the advantages and disadvantages of dilute acid and enzymatic hydrolysis.

Table 1.3
Comparison of enzymatic and dilute acid hydrolysis (Taherzadeh and Karimi, 2007).

Enzymatic hydrolysis	Dilute acid hydrolysis
Conditions (low *T*) are mild	High temperature and low pH
High yields of hydrolysis	Low yields of hydrolysis
Product inhibition during hydrolysis	No product inhibition during hydrolysis
No formation of inhibitory byproduct	Formation of inhibitory byproduct
Expensive enzymes	Solvent is cheaper than enzyme
Lengthy time for hydrolysis	Short time for hydrolysis

With enzymatic hydrolysis, it is possible to achieve nearly 100% cellulose hydrolysis to glucose, which is not possible with acid hydrolysis (Ogier et al., 1999). In comparison to acid hydrolysis, problems of inhibitory compounds formation are not severe for enzymatic hydrolysis (Lee et al., 1999; Taherzadeh, 1999). The main limitation is the high price of enzymes, which is much higher than the cost of acids, e.g. sulfuric acid (Sheehan and Himmel, 2001).

1.2.3 Pyrolysis oil upgrade technology

To be used as a substitute for fossil fuels, various deleterious properties of the bio-oil must be addressed, including high oxygen content, high viscosity, thermal instability, and corrosiveness. Two main processes are used to reduce the oxygen content

and upgrade bio-oil for use as a transportation fuel: (1) catalytic cracking, and (2) hydrodeoxygenation (HDO).

1.2.3.1 Catalytic cracking technology

Catalytic cracking converts pyrolysis bio-oil to smaller hydrocarbon molecules by catalytically removing oxygen as (1) H_2O (dehydration), (2) CO_2 (decarboxylation), or (3) CO (decarbonylation) under atmospheric pressure and in the temperature range of 300 to 600 ^oC (Kersten et al., 2007). Catalytic cracking does not require hydrogen co-feeding, as it is performed under atmospheric pressure, but it requires a long residence time for deoxygenation (Huber et al., 2006). However, some researchers co-fed hydrogen to test the effects on upgraded product and catalyst deactivation during catalytic cracking (Gayubo et al., 2009; Ausavasukhi et al., 2009).

Both zeolites and metal oxides have been used for catalytic cracking and upgrading of bio-oil. Zeolites, crystalline microporous inorganic material with pore structures of 0.5−1.2 nm, are popular catalysts in oil refining, petrochemistry and specialty chemical production (Stocker, 2005; Bekkum et al., 2001; Corma, 2003). Advantages of using zeolite catalysts are their large surface area, controlled adsorption and capacity, and usage as either hydrophobic or hydrophilic materials (Xu et al., 2007; Corma and Huber, 2007). Effects of temperature using HZSM-5 catalyst to upgrade bio-oil (Figure 1.2), showed that oil yield decreased, gas yield increased, and oxygen content was reduced with increasing temperature (Williams and Horne, 1994). This is caused by the increased rate of cracking that resulted in degradation of the bio-oil to light gases and carbon.

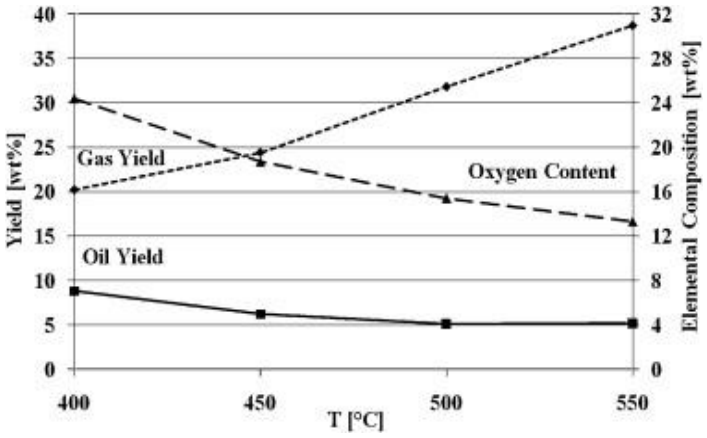


Fig. 1.2. Oil, gas and oxygen content as a function of temperature during bio-oil cracking using an H-ZSM-5 zeolite catalyst (Williams and Horne, 1994).

The activity and product distribution from zeolite cracking depend on the (1) availability of acid sites on zeolites, (2) pore size of the zeolites, and (3) decomposition and oligomerization reactions during cracking (Adjaya and Bakhshi, 1994; Vitilo et al., 2001). High availability of acid sites on zeolites results in massive hydrogen transfer, and therefore, a high gasoline fraction is obtained. In alumina-silicate zeolites, the availability of acid sites depends on the Si/Al ratio, where a high ratio indicates few acid sites because of few alumina atoms (Huang et al., 2009). Product distribution is influenced by pore size of zeolites. For smaller pore size (ca. 0.5−0.6 nm) zeolites, there is increased production of C_6−C_9 compounds, whereas for larger pore size (ca. 0.6−0.8 nm), production of C_9−C_{12} is greater during deoxygenation of bio-oil (Chiang and Bhan, 2010). During oligomerization reactions in zeolite, carbenium ions are formed, which is essential for cracking mechanisms, because the final product (mixture of aliphatic and aromatic hydrocarbons) depends on these reactions (Vitilo et al., 2001).

1.2.3.2 Catalysts for catalytic cracking

Several studies have assessed bio-oil upgrading using different catalysts for catalytic cracking technology (Table 1.4). In most cases, zeolite cracking of bio-oil has shown oil yields in the range of 14−23 wt% (Balat et al., 2009). Studies that used H-ZSM-5 catalyst for bio-oil upgrade produced as much as 30% aromatics (naphthalene, ethylbenzene and xylenes) from oxygenates in the product (Carlson et al., 2009; Carlson et al., 2011). Pore structure and acid sites on these catalysts are important for aromatic production in the product. For example, using H-ZSM-5 gave higher yields of aromatics than did silicalites because of more numerous acid sites on H-ZMS-5, even though pore structures were the same (Perego and Bosetti, 2011). Therefore, product selectivity results from the active sites and pore structures of catalysts (Carlson et al., 2008).

Other commonly used catalysts include H-Y zeolite, H-mordenite, silicalite, silica/alumina, SAPO 5, and SAPO 11 (Corma et al., 2007; Guo et al., 2011; Perego and Bosetti, 2011). In comparison to ZSM-5, any of these listed catalysts produce relatively large amounts of aliphatics and small amounts of aromatics (Perego and Bosetti, 2011). The bio-oil product from H-Y zeolites consisted of one-phase organic compounds that dissolved in water, whereas H-ZSM-5 produced separable organic and aqueous phases (Vitilo et al., 1999). Product yield was low for H-Y zeolite cracking processes, because high amounts of CO_2, CO, light alkanes, and light olefins were lost to the gaseous phase in comparison to H-ZSM-5. However, coke (6–29 wt% of feed), char (12–37 wt% of feed), and tar (12–37 wt% of feed) formation were high when upgrading with zeolite catalytic cracking, relative to other hydrotreatment processes.

Table 1.4
Studies of bio-oil upgrading using catalytic cracking technology.

Catalyst	Products	Limitations	References
HZSM-5	20−30% aromatic 7−30% olefin	catalyst lifetime reactor specific	Carlson et al., 2009; Carlson et al., 2011
ZSM-5 with Ni, Co, Fe, Ga, Zn, Ga	16% hydrocarbon 13 to 24 wt% O_2	poor fuel quality	French et al., 2010; Antonakou et al., 2006
Al/Cu-MCM-41 CuO, ZnO	phenol reduction acetic acid & furan increase	carbon formation short catalyst life	Adam et al., 2005; 2006; Gayubo et al., 2009
H-Y zeolite, SAPO 5 & 11	aliphatics low product yield	coke, char, & tar formation	Corma et al., 2007; Guo et al., 2003
HZSM-5	92 wt% organic, 47 wt% gasoline range	yield loss (CO, CO_2, H_2O)	Vargas et al., 2008
HZSM-5 co-fed with H_2 CsNaX in H_2	increased toluene production paraffin production	Deactivation	Ausavasukhi et al., 2009; Zhu et al., 2010

1.2.3.3 Hydrodeoxygenation (HDO) technology

Bio-oil is treated at temperatures of 300 to 600 ^{o}C in the presence of a heterogeneous catalyst and high pressure (76 to 300 bar) hydrogen for hydrodeoxygenation upgrade of bio-oil (Corma et al., 2007; Mercader et al., 2010). Operating conditions of high-pressure hydrogen resulted in high hydrogen solubility in oil (35−420 mol H_2/kg bio-oil), increased reaction rate, and decreased reactor coking problems (Elliot et al., 2009; Kwon et al., 2011). For operating temperature, Elliot et al. (2003), using Pd/C catalyst, showed that temperature increase from 310 to 340 ^{o}C increased HDO by 10%, but above 340 ^{o}C, HDO decreased (Elliot et al., 2009; Su-Ping et al., 2003). Significantly higher temperature was required for more complexly bound

oxygenated compounds like furans or ortho-substituted phenols for HDO on the basis of reactivity of different compounds as shown below (Furimsky, 2000).

Alcohol>ketone>alkylether>carboxylic acid
≈Substituted phenol>naphtol>phenol>diarylether
≈Substituted phenol>alkyl furan>benzofuran>dibenzofuran

Highly reactive compounds, such as ketones, are easily hydrogenated with little hydrogen. However, more stable oxygen-bound compounds, such as dibenzofuran, require high hydrogen consumption for high degrees of deoxygenation. During HDO, hydrogen reacts with oxygen to form water, which saturates C-C bonds and increase the energy content of the oil. Importantly, there is a decrease in oil yield because the removal of water and some gas production during the deoxygenation process (Figure 1.3). Significant oil yield decrease from 50 to 30% was reported when the degree of deoxygenation $\left[\left(1-\frac{\text{wt\% in product}}{\text{wt\% in feed}}\right) \text{x } 100\%\right]$ increased from 78 to 100%, using Co-MoS_2/Al_2O_3 catalyst (Samolada et al., 1998).

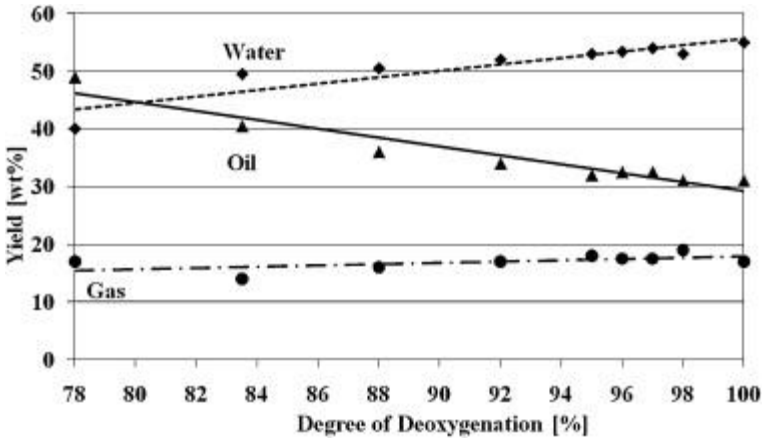


Fig. 1.3. Yields of oil, water, and gas from a HDO process as a function of the degree of deoxygenation over a Co–MoS_2/Al_2O_3 catalyst (Mortensen et al., 2011).

1.2.3.4 Catalysts for hydrodeoxygenation

Bio-oil upgrade results have been reported for different catalysts using HDO technology (Table 1.5). Ideally, hydrogenation of aromatics in bio-oil should be avoided during HDO, because this would decrease octane number and increase hydrogen consumption (Huber et al., 2006). Most research in this area was conducted with sulfided-NiMo-and-CoMo that were used on petrochemical feedstocks to remove sulfur, nitrogen, and oxygen (Elliot et al., 2009; Badawi et al., 2011; Bui et al., 2011). In these catalysts, Ni or Co act as promoters, donating electrons to molybdenum that weakens the sulfur and molybdenum bond; as a result, sulfur vacancy sites are created for both HDO and HDS reactions (Ferrari et al., 2001; French et al., 2010; Gandarias et al., 2008; Nava et al., 2009). Activity of both sulfide and oxide type catalysts depends on the acid sites available. When unsupported MoO_3 and MoS_2 were compared for HDO, MoO_3 had a lower activity and higher activation energy than MoS_2 (Bui et al., 2011). However,

oxides of W and Ni-W on active carbon indicated of high HDO in model compounds, such as 1 wt% phenol in *n*-octane (Echeandia et al., 2010).

Table 1.5
Studies of catalytic upgrading of bio-oil using hydrodeoxygenation technology.

Catalyst	Product	Limitation	Reference
Sulfided Co-Mo/Al_2O_3 Sulfided Ni-Mo/Al_2O_3	40% refined oil 1 wt% O_2	20 to 30% C lost in gas Gum formation Catalyst stability	Elliot and Neuenschwander, 1996 Elliot et al., 2007
Sulfided Co-Mo-P/Al_2O_3 MoO_3 & MoS_2	42 to 3 wt% O_2 reduction Prod oil soluble	equipment complication not scalable tetralin usage	Zhang et al., 2005 Kwon et al., 2011 Bui et al., 2011
Sulfided Co-Mo/y-Al_2O_3 Sulfided Ni-Mo/y-Al_2O_3	O_2 removal from carboxylic group	model compound usage (methyl heptanoate) excessive cost	Senol et al., 2005 Badawi et al., 2011
Pd/C, Pd/ZrO_2	21 to 10 wt% O_2 reduction 48 to 65% oil yield	drastic oil yield decrease expensive	Elliot et al., 2009 Wildschut et al., 2009
Ru/Al_2O_3,Ru/C Ru/TiO_2	higher DO than Co or Ni-MoS_2 High oil yield	good for batch expensive	Venderbosch et al., 2010 Wildschut et al., 2009
Pt/Al_2O_3/SiO_2 Pt/ZrO_2	*In situ* H_2 prod steam reformation	catalyst deactivation expensive	Gutierrez et al., 2009

For hydrodeoxygenation processes, other research includes Pt/Al_2O_3-SiO_2, Ru/C or Al_2O_3, and Pd/Ca or ZrO_2 catalysts (Wildschut et al., 2009; Gutierrez et al., 2009). Metals provide hydrogen donating sites, but oxy-compound activation was proposed at the metal sites or support interface (Mallat and Baiker, 2000; Vargas et al., 2008).

Studies of noble metal catalysts showed activities in decreasing order of Rh, Pd, and Pt on ZrO_2 used for HDO of 3 wt% guaiacol in hexadecane (Gutierrez et al., 2009), whereas Ru, Pd, and Pt on C using bio-oil showed high HDO and oil yields in a batch system (Wildschut et al., 2009). Although these metal catalysts had the potential to be HDO catalysts, their high prices make them unattractive. On the other hand, base metal catalysts (Ni-Cu/Al_2O_3, Ni/Al_2O_3, Ni-Cu/CeO_2) were successful in eliminating oxygen in anisole and were more economical than the metal catalysts discussed. However, their activity and affinity for carbon formation in comparison to metal catalysts were not investigated. Overall, the choice between sulfur-containing or noble metal catalysts needs further investigation to assess their potential for HDO of bio-oil.

1.3 Problems with the current conversion technologies

There have been many studies of biological/biochemical and thermal (pyrolysis) conversions of biomass to biofuel. In studies of biological conversions, many aspects of ethanol production from biomass (e.g., sorghum) have been investigated over the past two decades. The following factors are significant to this research; (1) effects of agricultural practices on sweet sorghum performance to improve soil and water conservation (Buxton, 1999), (2) different harvest approaches (Worley and Cundiff, 1991), (3) effects of juice processing techniques (Reidenbach and Coble, 1985) on juice recovery and ethanol yield, and (4) performance of different yeast strains on ethanol production (Phowchinda and Strehaiano, 2009). Other past research was directed at improving expression of various microbes. The expression and secretion of β-glucanase from *Trichoderma reesei* that hydrolyzes cellobiose and short oligosaccharides

facilitates the utilization of cellulose, and improves filterability of the spent medium (Penttila et al. 1988). Yet, current technologies suffer from problems in the biomass conversion processes, including high cost of enzymes, loss of sugars through corrosive chemical pretreatment, inability to utilize all sugars during fermentation, waste product formation, and lengthy fermentation times (Zaldivar et al., 2001; Hill et al., 2006).

In the area of thermal conversion (pyrolysis), extensive research has been conducted in the following directions: (1) improving biomass such as switchgrass productivity for pyrolysis, including management field trials, breeding, tissue culture, and physiological or genetic modifications (McLaughlin and Kszos, 2005); (2) production, reactor design, and pyrolysis conditions (Allen et al., 1995; Bridgewater, 2003); (3) product characterization (Oasmaa and Sipila, 1996; Lagernas, 1995), quality improvement (Sipila et al., 1998; Chiaramonti et al., 2003), and utilization (Bridgewater, 1994); and (4) feasibility of bio-oil generation by pyrolysis, with the goal of using it as transportation fuel (Williams and Horne, 1994). However, few studies have fully characterized the pyrolysis process and all the products resulting from pyrolysis at different temperatures. By characterizing the pyrolysis process and its products (bio-oil, syngas, and bio-char), the chemical composition and physical behavior of bio-oil can be better understood for further upgrading studies.

In the areas of bio-oil upgrade techniques, which includes bio-oil catalytic cracking using zeolites and metal oxides and HDO using moderate temperatures (300−600 °C) and high pressure in presence of hydrogen and heterogeneous catalysts, there are various limitations that need attention. Carbon deposition resulting in catalyst

deactivation is the main limitation of zeolite catalysts. In studies of pore blockage, high-molecular-weight compounds (mainly aromatics) had low reactivity on H-ZSM-5 and resulted in rapid zeolite deactivation (Guo et al., 2011). Even though catalytic cracking is considered a cheaper route compared to HDO for oxygenate conversion to lighter fractions, in most studies, results were not promising because of high coking (8−25 wt%) and the poor quality of fuel obtained (Zhang et al., 2007). Deactivation of catalysts is also a major problem of HDO. Past studies with Co-MoS_2/Al_2O_3 showed that active sites on the catalyst were blocked because of carbon formation from polymerization and polycondensation reactions, resulting in aromatic compounds on the catalyst surface for HDO (Furimsky and Massoth, 1999; Fonseca et al., 1999). Both feed composition (presence of organic acids) and process conditions affected the carbon formation during HDO. Therefore, bio-oil upgrade processes must be improved before HDO or zeolite cracking can be used on an industrial scale. These processes requiring improvement include; (1) decrease in process temperature, (2) decreases hydrogen usage and sustainable sources for the hydrogen used, (3) reduction of carbon or gum formation during bio-oil upgrade, (4) technically sound and cost effective catalyst development and lifetime, (5) understanding of kinetics of HDO of bio-oil or model compounds, (6) degree of deoxygenation needed for the final product, and (7) influence of bio-oil impurities on catalysts.

1.4 Goal, objectives, and hypotheses

Based on the limitations discussed in Section 1.3, this research utilized a combination of pretreatments without enzymes or chemicals to break down the lignin

structure and further used a combination of enzymes to optimize biomass conversion to sugars and ethanol. The pretreatment used in this research is beneficial because there are no high-cost enzymes or corrosive chemicals used, which can degrade sugars or produce inhibitors. The commercial enzymes used in combination also help optimize of bio-ethanol yield. For thermal conversion of lignocellulose (switchgrass), detailed characterization of all the pyrolysis products can be useful in developing novel upgrading technology, where bio-oil is upgraded to transportation biofuel (gasoline). A novel pathway focuses on (1) converting objectionable oxygenates (peroxide, aldehyde, ketone, carboxylic acid) to stable oxygenate like alcohol for a stable fuel; (2) converting di/tri olefins to mono-olefins to reduce gum problem; and (3) hydrogenating reactive and unstable compounds like styrene or indene to ethyl benzene/cyclohexane and indane, respectively, resulting in a stable fuel, unlike previous studies that mostly focused on removing oxygen. This unique pathway produces little water, no carbon monoxide, and carbon dioxide, resulting in no yield loss in the final product. Further, a comparison study of biological and thermal conversions will lead future work to decide a feasible route for biofuel production, based on feedstock characterization and mass and energy balance of the process. Figure 1.4 shows the approaches taken in this work for biofuel production from biomass.

The primary goal is to compare biological and thermal (pyrolysis) conversion pathways for biofuel production from various lignocellulosic feedstocks.

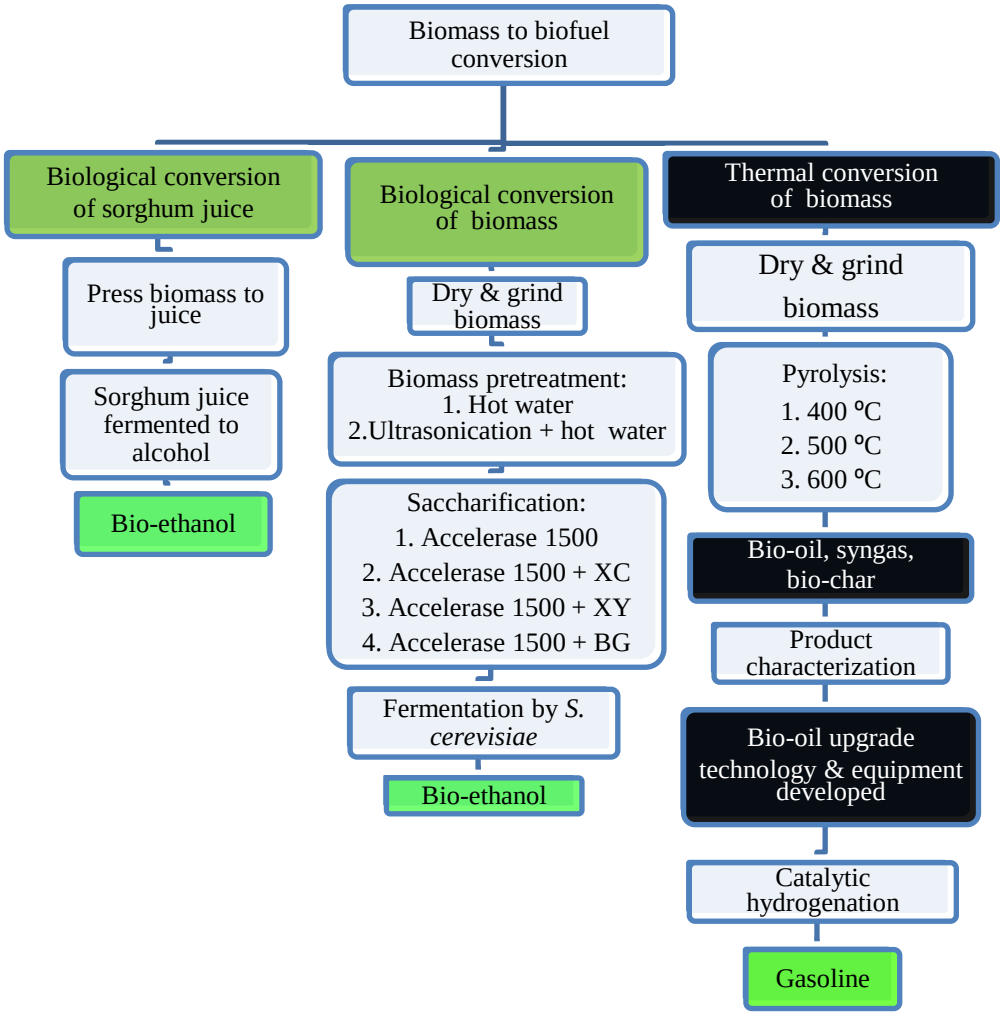


Fig. 1.4. Biomass to biofuel production approaches in this work.

The research objectives follow;

(i) Optimize bio-ethanol production through biological conversion of first- and second-generation biomass and determine the optimum conditions for pretreatment and enzymes for hydrolysis.

(ii) Optimize bio-oil production through thermal conversion (pyrolysis) of lignocellulosic biomass, and develop a novel pathway for bio-oil upgrade to produce transportation fuel, gasoline (C_5−C_{10}).

(iii) Compare biological and thermal conversion pathways in relation to feedstock characterization, process efficiency, and cost

The hypothesis follows:

Through biological conversions, bio-ethanol production can be optimized for first-and second-generation feedstocks by utilizing optimum conditions of pre-fermentation processes, combination of pretreatments (ultrasonic and hot water pretreatment), and combination of enzymes for lignocellulose conversion to sugars. Also, pyrolysis performed in an ideal temperature range optimizes bio-oil production, which can be upgraded to transportation fuel. Mass and energy distribution for biological and thermal process and feedstock characterization are important for validating process feasibility.

2. BIO-ETHANOL PRODUCTION FROM SWEET SORGHUM JUICE AND LIGNOCELLULOSE; OPTIMIZATION AND COMPARISON OF PRETREATMENTS AND SACCHARIFICATION[*]

2.1 Introduction

Bio-ethanol is a renewable fuel that can be produced from agricultural feedstocks such as sugarcane (Lorber et al., 1984; Thompson, 1979), sorghum (Gnansounou et al., 2005; Bailey, 1996), potato (Warren et al., 1986; Thornton, 1939), manioc (Laluce and Mattoon, 1984; Erratt and Stewart, 1981), and maize (Potter et al., 1995; Akpan et al., 2005). Concerns about ethanol production and its use relate to the large amount of arable land required for crops (Banat et al., 1998; Hossein et al., 2006). Conversely, the reduced energy usage and pollution from bio-ethanol as an eco-friendly alternative fuel usage are important (Almodares and Hadi, 2009). Small amounts (10%) of ethanol added to automotive gasoline can reduce greenhouse emissions like carbon monoxide and nitrogen oxides (Schaffert, 1992; Reddy et al., 2005).

Sweet sorghum (*Sorghum bicolor* (L.) *Moench*) is attractive for bio-ethanol production for the following reasons: (1) high yields of fermentable sugars and green biomass; (2) low requirement for fertilizer; (3) high efficiency in water usage; (4) short growth period with an adaptability to diverse climate (Hons et al., 1986; Wu et al., 2010) and tolerance to drought, water logging, soil salinity, and acid toxicity (Jasberg et al., 1983; Jackman, 1987). Also, compared to other crop residues, sorghum stover contains

[*]Reprinted with permission from "Ultrasonic and high temperature pretreatment, enzymatic hydrolysis and fermentation of lignocellulosic sweet sorghum to bio-ethanol" by Tahmina Imam and Sergio Capareda, 2012. International Journal of Ambient Energy, 33(3), 1−9, Copyright [2012] by Taylor & Francis.

lower lignin content, and requires less energy input for conversion to bio-ethanol (Schmer et al., 2008; Bryan, 1990). Moreover, it may be used as feedstock for jiggery syrup, as well as bio-ethanol (De Mancliha et al., 1984; Rao et al., 1983). The sugar content in the juice extracted from sweet sorghum varies from 16−24% Brix, depending on location grown (Rains et al., 1990; Imam and Capareda, 2011), and the juice is composed of sugars: sucrose, glucose, and fructose. The total available sugars may vary from 7.1−8.2 Mg/ha in sweet sorghum (Woons, 2000; Hoffman and Weih, 2005). Current research on sweet sorghum hybrids is focused on crossing grain-type seed parents and sweet-type pollen parents to increase the biomass yield and sugar content compared to the original parents (Hoffman and Weih, 2005; Miller and McBee, 1993). To improve economic value and ethanol yield, increasing the juice yield from the sorghum plants and using the remaining sugars in the lignocellulose are both crucial.

Sorghum biomass contains cellulose, hemicellulose, and lignin. Successful lignocellulosic conversion and optimization of the process greatly depend on pretreatment method, biomass properties, and microorganism efficiency (Dien et al., 2006; Dien et al., 2009). The ability to utilize all sugars present in lignocellulose continues to be a challenge in efficient production of ethanol. The following investigations were performed: (i) brown midrib (bmr) mutant sorghum, a naturally occurring mutation that results in plants with lower levels of lignin and treatment of crops with dilute acid and enzyme hydrolysis (Palmer et al., 2008; Sattler et al., 2009); (ii) use of fungal species, *Neurospora crassa* and *Fusarium oxysporum* to directly ferment cellulose to bio-ethanol (Deshpande et al., 1986; Lezinou et al., 1994); and (iii)

digest hemicellulose by converting xylose to xylulose for ethanol fermentation by yeast (Chiang et al., 1981; Chandrakant and Bisaria, 2000).

Other research has been directed at improving expression of various microbes. The expression and secretion of β-glucanase (enzyme that hydrolyzes cellobiose and short oligosaccharides from *Trichoderma reesei*) improved the utilization of cellulose, and filterability of the spent medium (Penttila et al., 1988). Further, genes for endo/exo-glucanase and β-glucosidase have been chromosomally integrated into a strain of *S. cerevisiae* L2612δGC that can produce ethanol in cellulose-containing media (Cho et al., 1999; Howard et al., 2003). Yet, current technologies continue to suffer from low ethanol yields, the need for severe pretreatment reaction conditions, incomplete sugar conversion to ethanol from microbe inefficiency, and requirement of large capital investments (Zaldivar et al., 2001). Clearly, for efficient biofuel production, improved technologies are needed to utilize the complete biomass (lignin, cellulose, and hemicellulose).

An objective of this research is to optimize bio-ethanol production through biological conversion of first- and second- generation biomass. First, two varieties of sweet sorghum juice (Umbrella, Variety 1 (V-1) and M-81E, Variety 2 (V-2)) that contained 14 to 15% sugars as fermentation substrates were evaluated for ethanol production. Pre-fermentation conditions of autoclaved juice, non-autoclaved juice direct from the refrigerator, and room temperature juices containing 25% and 30% sugar were compared for optimum ethanol production. A second objective is to optimize conversion of the lignocellulosic sweet sorghum biomass to bio-ethanol through ultrasonic and

pressurized high-temperature water pretreatment, followed by enzymatic hydrolysis by a mixture of enzymes and fermentation by *Saccharomyces cerevisiae.* Two pretreatment methods and different enzyme combinations were compared to optimize the percentage of lignocellulose converted to glucose and pentose sugars. Finally, based on the differences in the lignocellulosic conversion, ethanol production for the sweet sorghum biomass was determined for the different methods.

2.2 Materials and methods

2.2.1 Substrate

Two varieties of sweet sorghum (V-1 and V-2) were obtained from the Sorghum Breeding, Soil and Crop Sciences Department, Texas A&M University, College Station, TX. These Texas-grown plants were pressed to obtain the juices, which were refrigerated immediately. The juice yield from pressing the plants was 40%−50% (Wu et al., 2010). V-1 contains 64% sucrose, 22% glucose, and 14% fructose, whereas V-2 contains 56% sucrose, 30% glucose, and 14% fructose as determined by the high-performance liquid chromatography (HPLC) method (Section 2.2.7). Table 2.1 describes the content of each variety of juices.

Table 2.1
Sucrose, glucose and fructose content in V-1 and V-2 sweet sorghum juice.

Sugar Composition	V-1 Concentration (g/L)	V-1 Composition (%)	V-2 Concentration (g/L)	V-2 Composition (%)
Sucrose	89 (±2)	64	83 (±5)	56
Glucose	31 (±3)	22	44 (±1)	30
Fructose	20 (±1)	14	21 (±2)	14
Total sugars	140 (±6)	-	148 (±8)	-

Dry milled samples of sweet sorghum stalks were used for the lignocellulose to- ethanol conversion (Figure 2.1). This dry-milled sorghum was ground further in a Wiley mill to obtain an average particle size of approximately 1-mm diameter. The biomass had a moisture content of 8% as determined by ASTM D 3173.

Fig. 2.1. Sweet sorghum plants; first generation biomass, juice; second generation biomass, lignocellulose.

2.2.2 Enzymes

The enzymes used in this study were Accellerase 1500, Accellerase XC, Accellerase XY, and Accellerase BG, which were received from Genencor International, Incorporated. Accellerase 1500 was produced with a genetically modified strain of *Trichoderma reesei* and contained multiple enzyme activities: exoglucanase, endoglucanase, hemi-cellulase, and beta-glucosidase. Accellerase XC (an accessory enzyme was obtained from *Penicillium funiculosum*) and was used to improve both xylan and glucan conversion of lignocellulosic biomass. Accellerase XY (a hemicellulase enzyme) was obtained from a modified strain of *Trichoderma reesei* and was used to enhance various polysaccharide conversions of the lignocellulosic biomass.

Accellerase BG (a beta-glucosidase accessory enzyme) was obtained from a modified strain of *Trichoderma reesei* and was used to convert cellobiose to fermentable monosaccharides (glucose). Table 2.2 presents specifics of the enzymes, including enzyme activity, recommended dosages, and operational stability of the enzymes, as provided by Genencor International.

Table 2.2
Enzyme specifications.

Enzyme name	Enzyme activity*	Recommended dose	Operational stability
ACCELLERASE® 1500 (Cellulase enzyme)	Endoglucanase: 2200−2800 CMC U/g Beta-glucosidase: 525−775 pNPG U/g Total protein = 0.067 g/mL	0.05− 0.25 mL/g biomass added = 0.15 mL/g biomass activity added = 22.2 CMC U/g 5.28 pNPG U/g	Temp: 50−65 ^{0}C pH: 4.0−5.0
ACCELLERASE® XC (Xylanase/cellulase enzyme)	Endoglucanase: 1000−1400 CMC U/g Xylanase: 2500–3800 ABXU/g Total protein = 0.0913 g/mL	0.0125−0.125mL/g biomass added = 0.07 mL/g biomass activity added = 6 CMC U/g 17 ABX U/g	Temp: 45−65 ^{0}C pH: 3.5–6.5
ACCELLERASE® XY (Hemicellulase enzyme)	Xylanase: 20,000−30,000 ABXU/g Total protein = 0.029 g/mL	0.005 – 0.05 mL/g biomass added = 0.03 mL/g biomass activity added = 17.4 ABX U/g	Temp: 50−75 ^{0}C pH: 4.5−7.0
ACCELLERASE® BG (Beta-glucosidase enzyme)	Beta-glucosidase: 3000 pNPG U/g (min) Tot protein = 0.0452 g/mL	0.05−0.25 mL/g biomass added = 0.11 mL/g biomass activity added = 20.34 pNPG U/g	Temp: 50−65 ^{0}C pH: 4.0−5.0

2.2.3 Micro-organisms and culture media

The ethanol fermentations used dry alcohol yeast, *Saccharomyces cerevisiae* (Ethanol Red), provided by Fermentis (Lesaffre Yeast Corp., Milwaukee, WI) in vacuum-packed bags. These bags were stored in a refrigerator and were activated immediately before fermentation. Activation of dry yeast was accomplished by adding 0.5 g of dry yeast to 10 mL of preculture broth. Each 10 mL of the pre-culture broth contains 0.2 g glucose, 0.05 g peptone, 0.03 g yeast extracts, 0.01 g KH_2PO_4, and 0.005 g $MgSO_4.7H_2O$. The pre-culture broth was shaken at 200 rpm in an incubator shaker at 38 °C for 25−30 min.

2.2.4 Pretreatment

Two pretreatment procedures were performed on the 1-mm ground sample of lignocellulosic sweet sorghum biomass. One of the pretreatments involved two steps: (1) The ground cellulosic biomass was homogenized for 25 minutes using an Ultrasonicator presented on Figure 2.2 (Hielscher Ultrasonic Processors, Ringwood, NJ, USA). (2) The ultrasonicated samples were pretreated in a 2-L Parr pressure reactor (Parr Instrument Company, Moline, IL). The ground and homogenized sorghum biomass was mixed with water in a ratio of 1 to 9 wt/wt of biomass to water. The biomass and water slurries were loaded into the reactor and were treated at 150 ^{o}C for 30 min. The pretreated biomass was then washed with hot distilled water (100 ^{o}C) and centrifuged for 20 min at 12,000 rpm to remove the dissolved sugar from the pretreatment step. The supernatant from the pretreatment step was collected and analyzed by high-performance liquid chromatography (HPLC) (Section 2.2.7) to determine the sugar released during this step.

Most sugars released at this point are soluble sugars; some glucose could have been from the cellulosic part of the biomass (Corredor et al. 2007). The remaining portion was washed with water to ensure that soluble sugars did not influence final glucose or ethanol yields. This pretreated biomass was then subjected to enzymatic hydrolysis and fermentation. For the other pretreatment method, no ultrasonication was performed on the 1-mm ground biomass, which was taken directly to the pressure reactor following the above-mentioned pretreatment procedure. Summary of the pretreatment steps have been presented on Figure 2.3.

Fig. 2.2. Ultrasonication equipment used for pretreatment.

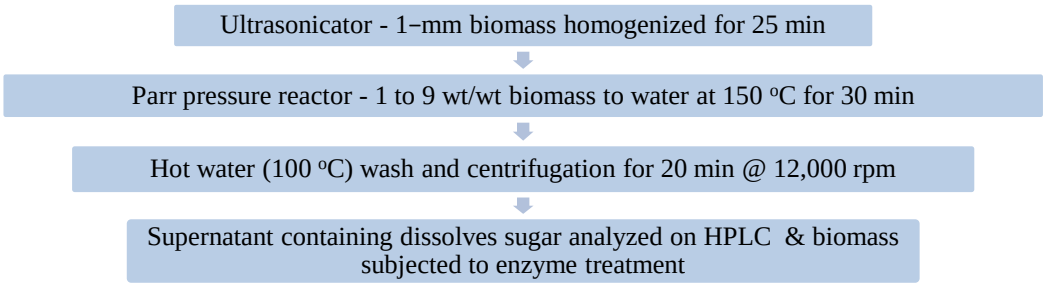


Fig. 2.3. Pretreatment steps summary.

2.2.5 Enzymatic hydrolysis

The pretreated biomass samples were enzymatically hydrolyzed in 50-mM sodium acetate buffer at pH 4.8 for 96 h. Hydrolysis was conducted at 50 ^{o}C at 125 rpm using an incubator/shaker (Innova, New Brunswick Scientific, NJ). There were four sets of enzymatic treatment experiments that included enzyme loading per g of dry biomass; (i) 0.15 mL/g of Accellerase 1500, (ii) 0.15 mL/g of Accellerase 1500 + 0.07 mL/g of Accellerase XC, (iii) 0.15 mL/g of Accellerase 1500 + 0.03 mL/g of Accellerase XY, and (iv) 0.15 mL/g of Accellerase 1500 + 0.15 mL/g of Accellerase BG. For soluble carbohydrates analysis, samples of hydrolysis slurries were collected at 0, 3, 6, 8, 24, 48, 72, and 96 h after enzyme addition. These sample slurries were centrifuged at 13,000 rpm for 20 min in a 1.5-mL auto-sampler vial, and the supernatant was filtered through 0.5-µm hydrophilic PTFE syringe filters (Millipore, Billerica, MA). Using HPLC, these filtered samples were then analyzed for sugar release during the enzyme hydrolysis procedure. Cellulose and hemicellulose conversion efficiencies were determined from the percentage of lignocellulose enzymatically converted to glucose, pentose, and other hexose sugars. Efficiency was calculated by comparing the hexose or pentose yield (g)

after enzymatic hydrolysis with the initial hexose or pentose content in the untreated biomass as follows:

$$\text{Lignocellulose to sugar conversion efficiency (\%)} = \frac{cV}{m} \times 100 \quad \text{------ (1)}$$

where, *c* is the concentration (g/L) of glucose or xylose in the sample hydrolyzed, as determined by HPLC during the enzymatic hydrolysis, *V* is the total volume (L) hydrolyzed, and *m* is the weight (g) of glucose or xylose before enzymatic hydrolysis determined through compositional analysis (refer to 2.2.7).

2.2.6. Fermentation process

Enzymatically hydrolyzed biomass was fermented with microbes (*Saccharomyces cerevisiae)* activated immediately before fermentation. To produce ethanol, these samples were subjected to fermentation to convert the glucose and other hexose released during pretreatment and enzymatic hydrolysis. A portion of the slurry (100 mL) was supplemented with 0.3 g of yeast extract. The pH was adjusted to 4.2 to 4.3 with 2-N hydrochloric acid. The slurry was then incubated anaerobically at 32 °C and 150 rpm with 1 mL of freshly activated dry yeast (Ethanol Red) and run for a period of 72 hours for ethanol production (Deshpande et al. 1986). All experiments were run in triplicate to determine the ethanol production from the variable, pre-enzymatic hydrolysis treatments. Samples were then centrifuged at 12,000 rpm for 15 min and the supernatant was analyzed for ethanol. In the biochemical conversion of sugar to ethanol, fermentation efficiency was calculated from the ratio between the average produced ethanol and the theoretical ethanol production i.e., 51.1 g of ethanol generated per 100 g of glucose consumed (Wu et al. 2006). Similarly, the sorghum juice obtained from

pressing the sorghum was first filtered using 25-mm Whatman 1005325 Grade 5 qualitative filter paper**.** Samples (1 L) of sorghum juice straight from the refrigerator were used to study the two varieties of juices. Fermentation efficiency was tested for autoclaved (30 min at 60 °C), non-autoclaved (frozen), 25% and 30% concentrated juice. The concentration of juice was increased by freezing the juice, allowing the water to rise and removing the ice from top. Then, the sugar content was measured by HPLC (Section 2.2.7) and diluted with deionized water if needed to maintain the required (25% and 30%) concentration under study.

2.2.7 Compositional analysis and analytical methods

For structural compositional analysis of the biomass (soluble sugars, cellulose, hemicellulose, lignin, and extractives), National Renewable Energy Laboratory (NREL) standard biomass analytical protocol was followed (Ruiz and Ehrman, 1996). Soluble sugars, structural extraction of biomass sugars; glucose, mannose, xylose, arabinose and ethanol concentration were determined by high-performance liquid chromatography (HPLC) (Waters 2690, Separations Module, Waters Corporation, Milford, MA) equipped with auto sampler, Shodex SP 810 packed column and a refractive index (RI) detector. Column temperature was maintained at 60 ^{o}C. Each sample was run for 25 min at a flow rate of 1 mL/min, using deionized water as the mobile phase. After mechanical pretreatment of ultrasonication, particle size was measured by Mastersizer 2000 (Malvern Instrument, Westborough, MA).

2.2.8 Parameter calculations

In the biological conversion of sugar, fermentation efficiency was calculated from the ratio between the average produced ethanol and the theoretical ethanol production of 51.1 g of ethanol generated per 100 g of glucose consumed (Wu et al., 2006). During the initial fermentation period of 4 to 18 h, the initial rates of sugar consumption S_m (g/(L·h)) and ethanol production P_m (g/(L·h)) were obtained from the slopes (a plot between sugar/ethanol (g/L) and time (h) of fermentation). Ethanol concentration P (% v/v) was the product concentration produced in the fermentation broth as determined by HPLC (Section 2.2.7). Ethanol yield, $Y_{p/s}$ (wt %), was calculated as ethanol produced per g of the different varieties of juice (Laopaiboon et al., 2009). Further, energy input in to the system will be calculated based on the biomass energy and the heat or electrical energy supplied to the system. Energy output would be the total energy from the products. Further, the energy loss in the system is the total energy output subtracted from total energy input.

2.3 Results and discussion

2.3.1 Ethanol production from first-generation biomass; sorghum juice

Ethanol production was studied using a 3-L fermenter reactor. Total sugar consumption in sorghum juice and ethanol production were measured during continuous fermentation. Figure 2.4 shows the total sugar consumption and ethanol production from V-1 and V-2 varieties of sorghum juice. At the end of 24 hours, the ethanol concentrations of V-1 and V-2 juices are 7.8% (±1%) and 8.5% (±1%) (Figure 2.4).

Figure 2.4 shows three stages. V-1 sorghum juice has a faster initial total sugar reduction and ethanol production than does V-2. For V-1, the initial decrease occurs after the second h, whereas for V-2, the initial decrease occurs after the sixth h. Therefore, it is easier for the inoculated yeast cells in V-1 to adjust to fermentation than for V-2. During the first 6 hours for V-2 sorghum juice, sugar consumption and ethanol production are low. This is explained by the differences in the proportions of the glucose and sucrose in the two varieties of juice (Table 2.1). For the initial stage of fermentation, starting with a higher concentration of mixed sugars is less efficient compared to a lower concentration of mixed sugars.

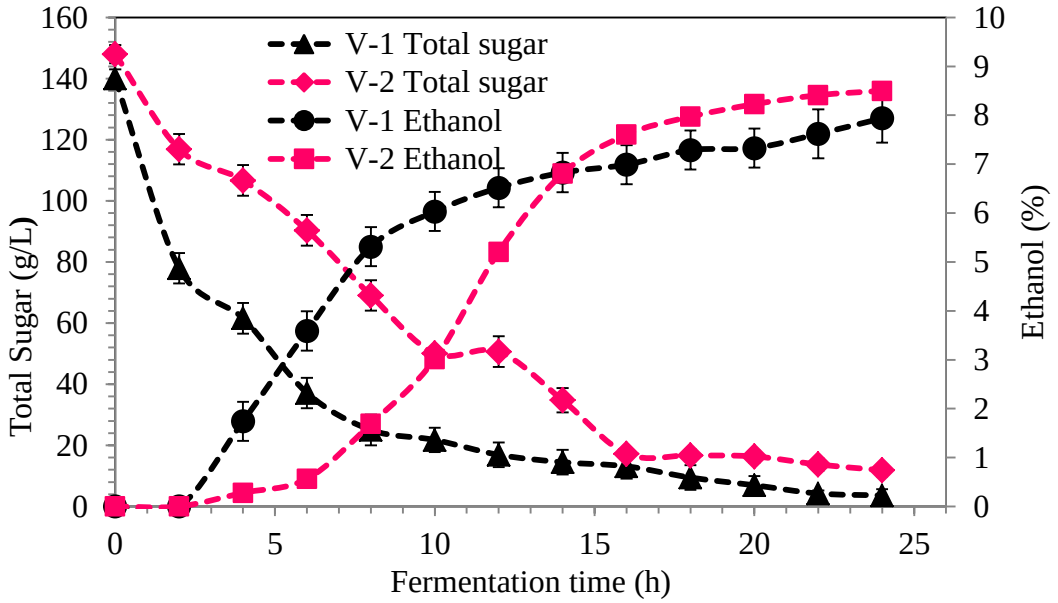


Fig. 2.4. Fermentation of V-1 and V-2 sorghum juice to ethanol by *Saccharomyces cerevisiae*, truncated at 24 h.

Most rapid glucose consumption and ethanol production occur between Hours 2 and 10 for V-1 and Hours 6 and 16 for V-2 sweet sorghum juice (Figure 2.4). Between the stated hours for V-1 and V-2, glucose consumption decreases and ethanol production increases nearly linearly. Even though most glucose seems to be absorbed by Hour 20 for V-1 and Hour 24 for V-2, ethanol concentration continues to increase slightly in both cases. This results because the remaining fermentable sugars were utilized; sucrose was hydrolyzed to glucose, and fructose, which resulted in ethanol generation after the initial glucose was consumed. At the final stage, the ethanol concentration increased very slowly because of slow release of glucose and fructose from residual sucrose. When this experiment was run for 72 hours, there was little/no change in ethanol production after Hour 24.

The following fermentation kinetic parameters were determined: maximum sugar consumption rate (S_m), maximum ethanol production rate (P_m), ethanol concentration (P), at the end of the fermentation period, and ethanol yield ($Y_{p/s}$) for both varieties of sorghum juices (Table 2.3). There were higher sugar consumption and ethanol production rates for V-1 juice than for V-2 juice (Table 2.3). During the first 18 hours of fermentation, the concentration of total sugars in V-1 juice decreased linearly at a rate of 3.3 g/L·h. For V-2, the linear decrease lasted nearly 22 hours with a maximum consumption rate of 2.2 g/L·h; thus total sugar consumption and ethanol production were faster for V-1 juice compared to V-2 juice. This may be caused by the lower sugar concentration (Table 2.1) in V-1 that allowed the yeast to readily consume the juice,

compared to the V-2 juice, which has slightly higher concentration of sugars.

Table 2.3
Fermentation kinetic parameters of ethanol production.

Variety	Max total sugar consumption rate, S_m (g/L·h)	Max ethanol production rate, P_m (g/L·h)	Max ethanol concentration, P (% v/v)	Ethanol yield, $Y_{p/s}$ (wt ethanol/wt sugar)
V-1	3.3	1.8	8.3	0.46
V-2	2.2	1.6	9.2	0.49

*Parameters calculated between 4 and 18 h when sugar consumption and ethanol production rapidly changed (Fig 2.4)

The maximum ethanol concentration, P in the fermentation broth was slightly higher for V-2 juice (9.2%) than for V-1 juice (8.3%), because of the slightly greater amount of initial sugar in V-2 than V-1 (Table 2.1). These results are comparable to those of Laopaiboon (2009) and Belloch (2008), who reported that most yeast strains can ferment juices containing 20% sugars, producing ethanol concentrations of 10% to 12% v/v with high fermentation efficiency. Also, the ethanol yield, $Y_{p/s}$ was greater for V-2 juice than V-1 juice (Table 2.3). The yield of 0.46 wt% for V-1 juice implied that, for every liter of V-1 juice (140 g sugars), 65 g ethanol was produced whereas for V-2 juice (148 g sugars), 72 g of ethanol was produced resulting in a yield of 0.49 wt%. This yield comparison between the different varieties of juice is important for ethanol production because sweet sorghum juice is being used as a substrate for ethanol production in many parts of the world.

2.3.2 Fermentation efficiency for various pre-fermentation juice processes

When fermentation was performed on autoclaved juice (20%), frozen juice

straight from refrigerator (20%), and various concentrated juices (25%, and 30%), fermentation efficiency differed (Figure 2.5). Fermentation efficiencies of frozen juices were higher than those autoclaved juices or highly concentrated juices (Figure 2.5). This can be explained by low bacterial contamination due to low pH (Warren et al., 1986) and low temperature. Also, adjusting the juice pH from 4.2 to 4.4 before yeast inoculation prevented contaminated bacteria from competing with yeast. Autoclaved juices may have lost some heat-sensitive nutrients and generated inhibitors that might have decreased fermentation efficiency (Rein et al., 1989). Concentrated juices had the lowest fermentation efficiencies. This may have been caused by the inhibiting effects of high ethanol concentration, aconitric acid, or the combination of both (Wu et al., 2010; Prasad et al., 2007).

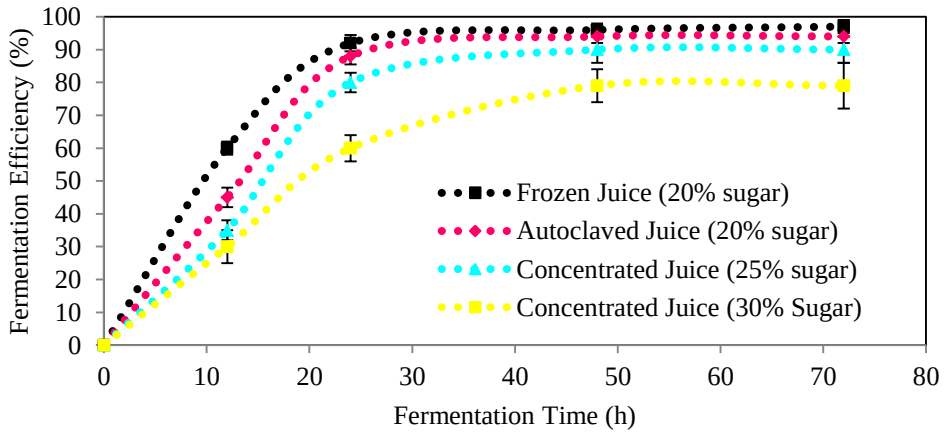


Fig. 2.5. Comparison of ethanol fermentation efficiency among the different juices processed.

From Figure 2.5, sorghum juices do not need to be autoclaved for better fermentation efficiencies; however, it is best to keep the sugar concentration below 25% for higher efficiency. Further, highly concentrated juices of 25% and 30% had residual sugars of 3% (±2%) and 10% (±5%), respectively (Table 2.4), containing mostly fructose and some sucrose. The frozen or autoclaved juice had negligible remaining sugars.

Table 2.4
Total residual sugars contents in the final product from concentrated juices.

Concentrated Juice	Residual Sugars (%)
25% Sugar	3% (±2%)
30% Sugar	10% (±5%)

Previous studies report that various other ingredients (e.g., glycerol and lactose) are more abundant in the high-concentration juice than in low-concentration juice, which may also have contributed to the lower fermentation efficiencies of the concentrated juices (Wu et al., 2010; Rein et al., 1989). The corresponding ethanol concentrations for the four pre-fermentation conditions presented in Figure 2.5 are 12−14%, 11−13%, 11−12%, and 9−10% for the non-autoclaved frozen juice, autoclaved juice, 25% juice and 30% juice, respectively. At the end of fermentation, all juices had fermentation efficiencies greater than 90%, except for the 30% juice. In comparison, for M81E varieties (V-2) of sweet sorghum juice from Riley and Doniphan counties in Kansas, Wu et al. (2010) reported fermentation efficiencies with different pre-fermentation processes, where frozen juice had the highest fermentation efficiency (94%). Also, they found

similar ranges of results for other conditions as observed in this study. In contrast, Rein et al. (1989) reported fermentation efficiencies of 41% for unheated raw juice and greater than 90% for autoclaved juice.

Based on the two varieties of sorghum juice, Table 2.5 summarizes the ethanol production per hectare of land. Compared to V-1, V-2 juice has approximately 10% higher ethanol yield per hectare of land. These results are similar to previously reported yields for sweet sorghum. Wu et al. (2010) reported ethanol yield of 2134−2470 L/(ha·yr) for M81-E (V-2) from sweet sorghum grown in Kansas. In comparison, Texas-grown V-2 sweet sorghum (this study) produced 1704−2273 L/(ha·yr) (Table 2.5). Similarly, sweet sorghum (variety unknown) grown in India yielded 2816−4052 L/(ha·yr) (Prasad et al., 2007). V-1 ethanol yield data are not readily available in literature, but this variety has a more rapid rate of ethanol production compared to V-2, even though the yield is lower.

Table 2.5
Approximate ethanol production per acre of land.

Variety	*Ethanol/hectare (L/(ha·yr))
1	1537−2050
2	1704−2273

*Assuming average growth of 15-20 dry tons of sorghum / acre (McCutchen, 2006)

The results in Table 2.5 may be used to compare efficiencies of ethanol production of sweet sorghum varieties to one another. Also, they may be used to assess the efficiencies

sweet sorghum varieties relative to other agricultural products, such as maize, sugarcane, and many others, for generating ethanol from biomass. Because of the ease of plant growth, V-1 may be more profitable than V-2 for ethanol production. V-1 is day-length insensitive, and it matures more rapidly, in general, than V-2. On the other hand, V-2 may be a better sweet sorghum option during the fall, because these plants are day-length sensitive.

2.3.3 Effect of pretreatment process on lignocellulosic biomass

Table 2.6 shows the chemical composition (wt%) of sweet sorghum is 14% soluble sugars (31% glucose, 14% fructose and 55% sucrose), 34% cellulose, 19.7% hemicellulose (xylan, arabinan, and mannan), all of which can be used to produce ethanol. Total components measured accounted for 88% of the dried biomass, and the residual material (not tested) included protein and minerals. The chemical compositions of untreated biomass were similar to those reported by Salvi et al. (2010). The composition of hot water pretreatment, and ultrasonic + hot water pretreatment, were significantly different from the untreated biomass results (Table 2.6). Respectively, cellulose and hemicellulose concentrations increased by 35% and 15% for the hot water treatment, and 49% and 25% for ultrasonic + hot water treatment, respectively.

Table 2.6
Effect of pretreatment process on biomass composition.

Components (%)	Untreated biomass	Hot water treatment[a]	Ultrasonicate + hot water treatment[b]
Soluble sugars	14	1.2	0.1
Cellulose	34	46	50.6
Xylan	16.5	19	21
Arabinan	3.0	3.2	3.2
Mannan	0.2	0.4	0.5
Lignin	11	11.4	5.7
Extractives	7	5.4	5.4
Ash	2.5	2	1.7

[a]Hot water treatment was performed at 150 ^{o}C for 30 min in a pressure reactor
[b]Ultrasonication was performed for 25 min prior to hot water treatment

When ultrasonic energy was used together with hot water, average particle size of the lignocellulosic biomass was reduced from 1 mm to 0.01 mm, thus increasing the surface area of the biomass particles. The lignocellulosic biomass was exposed to intense ultrasonic sound waves that propagated through the liquid, causing alternating high and low pressures to occur approximately 20,000 cycles/s (Hielscher - Ultrasound Technology, Ringwood, NJ). These pressure cycles generated high-pressure implosions, and high-speed liquid jets locally in the biomass. The resulting turbulences disrupted lignin structure. The lignin concentration decreased by 52% after the ultrasonic + hot water pretreatment (Table 2.6). Violent action disrupts the crystalline structure of cellulose, making it easily hydrolyzable for the next pretreatment step (Lezinou et al. 1994, Kumar et al. 2009).

The lignin-hemicellulose matrix that surrounds cellulose affects the accessibility of hydrolytic enzymes. Ultrasonic + hot water pretreatment mechanically and chemically breaks the lignin-hemicellulose barrier. The polysaccharides (pentan and hexan) in

hemicellulose and the cellulose became hydrated (Salvi et al. 2010, Kumar et al. 2009), which facilitates enzymatic hydrolysis. Further, ultrasonic + hot water pretreatment increased both cellulose and hemicellulose concentrations while reducing lignin. In comparison to acid or alkali pretreatment, hemicellulose is degraded and lost to a certain extent (Dien et al., 2009; Beismann et al., 1997). Various combinations of enzymes were tested on ultrasonic + hot water pretreated samples. Also, one high-efficiency enzyme was used to hydrolyze hot water treatment only.

2.3.4 Enzymatic hydrolysis efficiency of lignocellulose to hexose and pentose

After pretreatment, cellulose and hemicellulose were hydrolyzed to glucose and xylose by adding combinations of cellulase and hemicellulase enzymes. Further, glucose was converted to ethanol by *S. cerevisiae*. The enzyme loading for the data reported in Figure 2.6 are; A 1500 + XC (0.016 g protein/g biomass), A 1500 + BG (0.015 g protein/g biomass), A 1500 + XY (0.015 g protein/g biomass), A 1500 (0.01 g protein/g biomass) for all ultrasonic + hot water treated samples. Enzyme loading for A 1500 + XC that was only hot water treated was 0.016 g protein/g biomass. For the same protein loading, the difference between ultrasonication and no ultrasonication is presented by the cellulose to glucose conversion efficiency difference (Figure 2.6).

Figure 2.6 compares the enzymatic hydrolysis of cellulose to glucose by different enzyme combinations. The efficiency of cellulose conversion to glucose was greatest when Accellerase 1500 was used in combination with Accellerase XC enzyme (89%), followed by Accellerase 1500+BG (84%), and Accellerase 1500+XY (83%), and Accellerase 1500 (82%) were similar (Figure 2.6) after the 96 hours of saccharification

process. Such cellulose-to-glucose conversions were similar to those of Dien et al. (2009) and slightly higher compared to those of Corredor et al. (2007). Addition of Accellerase XC to Accellerase 1500 increased the cellulose conversion to glucose, because of its added endoglucanase activity. Similarly, Accellerase BG initially improved cellulosic conversion because of its beta-glucasidase activity. However, Accellerase BG's efficiency is lower compared to XC, because it also acted as an inhibitor to the Accellerase 1500 (Genencor Inc.).

When no ultrasonication was combined with hot water pretreatment, the enzymatic hydrolysis efficiency from cellulose to glucose was 71% with A1500+XC combined enzymes (Figure 2.6). Adding ultrasonication increased enzymatic hydrolysis efficiency by 10−15% to hot water pretreatment. Studies of Goshadrou et al. (2011) reported 16% difference between untreated sorghum biomass vs. ultrasonic + acid pretreated biomass, 3% difference between acid treated vs. ultrasonic + acid pretreated biomass, 27% difference between untreated biomass vs. ultrasonic + alkali treated biomass and no difference between ultrasonicated + alkali treated vs. alkali treated biomass during enzymatic hydrolysis of cellulose to glucose. From the literature and research results ultrasonic treatment improves hot water and acid pretreatments but not alkali pretreatments.

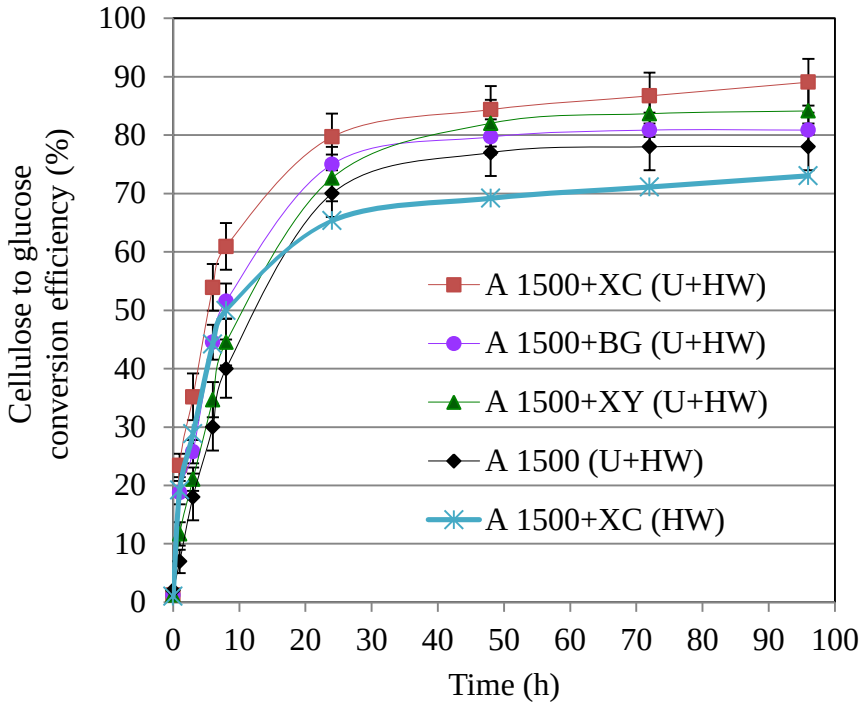


Fig. 2.6. Cellulose to glucose conversion efficiency by combined enzyme hydrolysis.
*U = ultrasonic pretreatment & HW = hot water pretreatment

Figure 2.7 compares the enzymatic hydrolysis of hemicellulose to xylose and arabinose by different enzyme combinations. The hemicellulose conversion to xylose and arabinose was the highest when Accellerase 1500 was combined with Accellerase XC enzyme (48%), followed by Accellerase 1500+XY (40%) after saccharification period of 96 hours. Both these hydrolysis was performed after ultrasonic + hot water pretreatment. These hemicellulose-to-pentose sugar conversions are similar to those of Corredor et al. (2007), but conversion results were lower than those of Dien et al. (2009). Both Accellerase XC and XY had xylanase activity that was combined with cellulases. Such enzyme functions are discussed in previous reports (Wooley et al., 1999; Wyman,

2001). Earlier research showed good yields of sugars from hemicellulose when biomass was treated with acid (Gnansounou et al. 2005, Dien et al. 2009). Because only hot water in combination with mechanical treatment was used in this research, the pentose sugar yields were low in comparison to acid pretreated samples from other studies (e.g., Laser et al. 2002). Further, when hot water pretreatment was performed in absence of ultrasonic pretreatment, hemicellulose conversion efficiency was lowered by 10% (Figure 2.7). The protein loading for each case was stated earlier, where only Accellerase XC and XY had hemicellulase or xylanase activity.

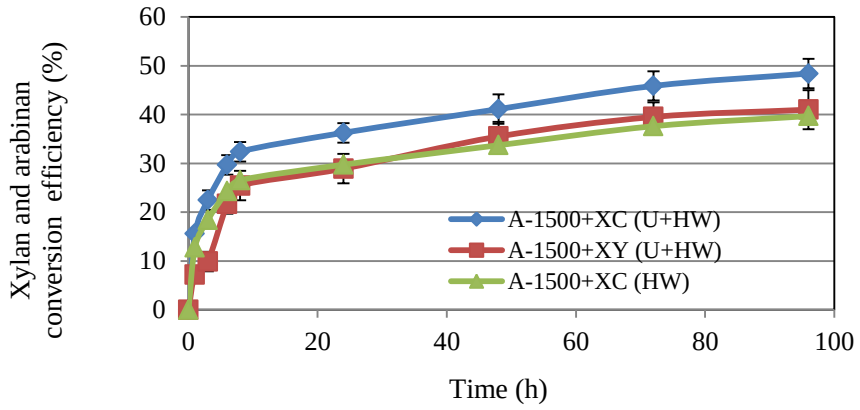


Fig. 2.7. Hemicellulose to xylose and arabinose conversion efficiency by combined enzyme hydrolysis.

For both cellulosic and hemicellulosic hydrolysis and fermentation, hot water pretreatment is preferred over acid or alkaline pretreatment, because hot water reduces fermentation inhibitors (e.g., acetic acid and furfural) released from biomass or produced by degradation reactions during acid or alkaline pretreatment, thereby improving the

hydrolysis process (Gnansounou et al., 2005; Beismann et al., 1997; Corredor et al., 2007). After pretreating biomass with cellulose and hemicellulose were hydrolyzed to soluble sugars (glucose, xylose, and arabinose) using the combination of cellulases and hemicellulases, the sugars were fermented to ethanol.

2.3.5. Cellulosic fermentation for ethanol production

The cellulosic part of biomass was fermented to ethanol by the mixed enzymes and *S. cerevisiae*. Only glucose from cellulose was converted to ethanol, because *S. cerevisiae* does not ferment pentose, which was 19.4% of the biomass. Figure 2.8 shows the effects of different enzymatic hydrolysis processes on ethanol production. Because the combined enzymes of Accellerase 1500 and Accellerase XC had a higher cellulosic conversion to glucose, ethanol production was also higher because of the greater amount of glucose available for fermentation. Following fermentation, the broth was analyzed for ethanol concentration, and ethanol yield was calculated on the basis of fresh sorghum biomass, where only the cellulosic part of the biomass was converted to ethanol. Based on cellulosic conversion, ethanol yield varied from 3.2 g to 4.2 g ethanol per 100 dry g of sweet sorghum biomass. These yields are similar to those of Mamma et al. (1995), but lower those of Bryan (1990). Ethanol yield was 10, 24, and 31% higher when Accellerase 1500+XC was used in comparison to Accellerase 1500+BG, Accellerase 1500+XY, and Accellerase 1500, respectively. Therefore, the yield was 17 to 22% of the theoretical ethanol yield from cellulosic biomass.

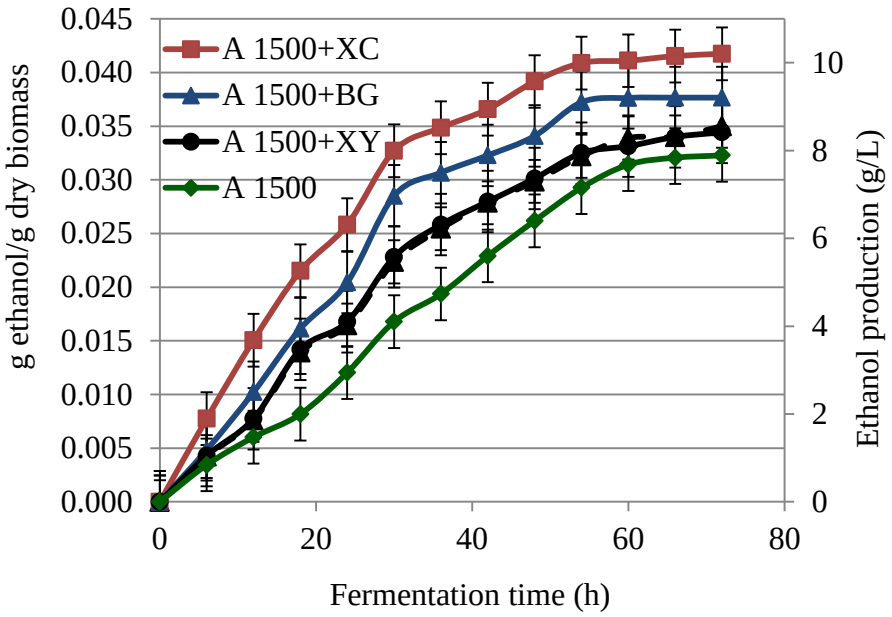


Fig. 2.8. Ethanol production from sorghum biomass using different enzymatic conversions and fermentation by *Saccharomyces cerevisiae* (based on cellulose only).

2.3.6 Ethanol production from first and second generation biomass

Based on this study, Table 2.7 presents ethanol production from sweet sorghum per hectare of land. Cellulose (34%) and soluble sugars (14%) are considered for ethanol yield calculations. Bennett and Anex (2008) reported average ethanol yield of 3,848 L/ha for sweet sorghum grown in Mississippi. In comparison, Texas grown sweet sorghum (this study) produced 2,285 L/ha from cellulose part of the biomass (Imam and Capareda, 2012) and 2,050 to 2,273 L/ha can be produced from the soluble sugars based on 90% conversion of the sugars. Therefore, combining both soluble sugars and cellulose provides 4,335 to 4,558 L/ha, which is slightly higher than Bennett and Anex's (2008) ethanol yield of 3,848 L/ha. The yield from this research would be higher if

hemicellulose (19.7%) sugars were converted to ethanol. Further, according to Hunter and Anderson (1997), ideally, all sugar produced in sweet sorghum has a potential ethanol yield, which would result in as much as 7,000 L/ha.

This study showed that using both Accellerase 1500 and Accellerase XC enzymes in combination with ultrasonic + hot water pretreatment is a potential process for converting lignocellulose to glucose and xylose, which in turn, can increase ethanol production. In this study, ethanol production could have been optimized if other microbes in combination with *S. cerevisiae* had been used to convert pentose to ethanol.

Table 2.7
Ethanol production comparison between experimental biomass and other feedstocks.

Feed stocks	Ethanol (L/ha·yr)	Reference
Sweet sorghum juice	1,537–2,273	Experimental (Imam and Capareda, 2011)
Sweet sorghum lignocellulose	4,335–4,558	Experimental (Imam and Capareda, 2012)
Sweet sorghum juice + baggase lignocellulose	3,134–3,870	Calculated based on (Imam and Capareda, 2011 and 2012)
Sweet sorghum lignocellulose	2,500–7,000	http://en.wikipedia.org/wiki/Ethanol_fuel
Corn	3,100-4,000	Goettemoeller, 2007
Sugarcane juice	6,000-8,000	Goettemoeller, 2007
Switchgrass	3,100-7,600	http://en.wikipedia.org/wiki/Ethanol_fuel

Table 2.7 present the efficiencies of sweet sorghum relative to other agricultural media, such as switchgrass, sugarcane, and corn for generating ethanol from lignocellulosic biomass and first-generation biomass. Corn and sugarcane (first-

generation biomass) compete with food and may not be considered a reliable option, even though they have a high yield of ethanol production per hectare of land. On the other hand, switchgrass and sweet sorghum (second-generation biomass) have similar ethanol yields per hectare of land, but do not compete with food. Further, being lignocellulosic biomass, they have a negative carbon balance to the environment (Reddy et al., 2005). However, the ease of plant growth, drought tolerance, water logging, and soil salinity, make sweet sorghum a prospective future source for both syrup and bio-ethanol production (Jasberg et al. 1983, Rao et al. 1983).

2.4. Conclusions

Ethanol production varies depending on the variety of sweet sorghum and the amount and proportion of sugar in the sweet sorghum. Rates of glucose consumption, ethanol production, and cell growth are higher at an optimal concentration sugar using a yeast specific to the substrate that should always be determined to optimize any fermentation process. In this study, V-1 had a smaller ethanol yield compared to V-2; however, rates of sugar consumption and ethanol production were higher for V-1 because of its initial lower concentration of sugar. This was verified by the fermentation parameters: maximum sugar consumption rate was 3.3 g/(L·h) for V-1 juice, and 2.2 g/(L·h) for V-2 juice, and maximum ethanol production rate was 1.8 g/(L·h) for V-1 juice and 1.6 g/(L·h) for V-2 juice. Ethanol concentration in the final fermentation broth was 8.3% for V-1 juice and 9.2% for V-2 juice. In terms of energy efficiency, V-1 may be a better crop because of its higher rate of ethanol production and shorter maturation. In terms of ethanol yield, V-2 (0.49 wt% ethanol/sugar) may be a better choice. Ethanol

fermentation efficiency varied among the four pre-fermentation preparations. Fermentation efficiencies for frozen, autoclaved, and juice containing 25% sugar were greater than 90%. In contrast, juice containing 30% sugar had lower efficiency (79%) because fermentation did not go to completion.

Pretreatment greatly influences conversion efficiency of the cellulose and hemicellulose. This research evaluated hot water pretreatment alone, and the combination of ultrasonic pretreatment + hot water pretreatment, which reduced both lignin and particle size of the biomass. The pretreatment of this study is advantageous over acid, alkali or other chemical pretreatments, because it reduced inhibiting compounds (e.g., furfural), and no chemicals were used. Cellulose and hemicellulose concentrations were increased by 35% and 15% with the hot water treatment and 49% and 25% with the combination of the mechanical plus hot water treatment, respectively. Lignin concentration decreased by 52% after ultrasonic + hot water pretreatment, whereas it increased by 1% when biomass was treated with hot water alone and did not undergo further homogenizing.

The efficiency of cellulose conversion to glucose was greatest when Accellerase 1500 was combined with Accellerase XC enzyme (89%) followed by Accellerase 1500+BG (84%), Accellerase 1500+XY (83%), and Accellerase 1500 (82%). The hemicellulose conversion to xylose and arabinose was greatest when Accellerase 1500 was combined with Accellerase XC enzyme (48%), followed by Accellerase 1500+XY (40%). There was an increase of 15% and 7% for cellulose to glucose and hemicellulose to pentose and hexose, respectively, when ultrasonication was combined with hot water

pretreatment versus only hot water treatment alone. Based on cellulosic conversion only, ethanol yield in this study varied from 3.2 g to 4.2 g ethanol per 100 g of dry sweet sorghum biomass. Ethanol yield was 10%, 24% and 31% higher when Accellerase 1500+XC was used in comparison to Accellerase 1500+BG, Accellerase 1500+XY, and Accellerase 1500, respectively. Using a mixture of Accellerase 1500 and Accellerase XC enzyme combined with mechanical and hot water pretreatments increased ethanol production. Ethanol production may be further increased if a pentose-fermenting microbe can be employed during fermentation. This study yielded 1,537−2,273 L ethanol/(ha·yr) for first-generation biomass (sweet sorghum juice), 4,335−4,558 L ethanol/ha·yr from whole lignocellulosic sweet sorghum biomass without xylose conversion to ethanol.

3. PYROLYSIS TEMPERATURES EFFECTS ON OPTIMAL BIO-OIL PRODUCTION AND CHARACTERISTICS OF BIO-OIL, SYNGAS AND BIO-CHAR FROM SWITCHGRASS[*]

3.1 Introduction

The US Department of Energy has designated switchgrass (*Panicum virgatum*), a high-yielding perennial grass, as an energy biomass for renewable sources of fuel and electricity generation (Missaoui et al., 2005; McLaughlin and Kszos, 2005; Lee and Fasina, 2009). Perennial grasses have various advantages over annual crops, such as lower establishment costs (McLaughlin et al., 2002), reduced soil erosion (Roth et al., 2005), increased water quality (Walsh et al., 2003), excellent conservation attributes, good compatibility with conventional farming practices (McLaughlin et al., 1999), and enhanced wildlife habitat (Adler et al., 2006). Also, there has been extensive research on improving switchgrass productivity, including management field trials, breeding, tissue culture and physiological or genetic modifications (McLaughlin and Kszos, 2005; McLaughlin et al., 2002). Switchgrass is a C_4 species, meaning CO_2 is fixed into oxaloacetate, which contains four carbon atoms in mesophyll cell before entering the Calvin cycle of photosynthesis. It has the anatomical and physiological characteristics of typical C_4 grasses (Boateng et al., 2006); therefore, it can better withstand drought, high temperature, and nitrogen limitations. Further, low water loss by

[*]Reprinted with permission from "Characterization of bio-oil, syn-gas and bio-char from switchgrass pyrolysis at various temperatures" by Tahmina Imam and Sergio Capareda, 2011. Journal of Analytical and Applied Pyrolysis, 93, 170−177, Copyright [2011] by Elsevier.

the plant allows it to grow for more than 10 years in an arid environment (Sage and Russell, 1999; Osborne and Freckleton, 2008).

Various pyrolysis oil combustion demonstrations have been performed, including applications such as boilers, diesel engines, and gas turbines (Czernik and Bridgewater, 2004; Shaddix and Hardesty, 1999). However, there are some problems with switchgrass bio-oil, including high: acidity, viscosity, water content, and inorganic content (Agblevor and Besler, 1996; Maggi and Delmon, 1994). Pyrolysis studies include the following; reactor design (Alen et al., 1995), pyrolysis conditions (Bridgewater, 2003), bio-oil characterization (Oasmaa and Sipila, 1996; Lagemas, 1995), quality improvement (Sipila et al., 1998; Chiaramonti et al., 2003), utilization (Bridgewater, 1994), and feasibility of the bio-oil from pyrolysis (Williams and Horne, 1994). On the other hand, pyrolysis co-products (bio-char and syngas) have many potential uses that add to the economic viability of the production of bio-oil as a fuel (Day et al., 2005; Soto et al., 2008; Bakkerud, 2005; Mills, 1994). Bio-char has several prospective applications, including enhancement of soil quality (Hansen et al., 2008), sequestration of carbon to mitigate global climate change (Laird, 2008), improvement of soil water and nutrients retention (Mullen et al., 2010), and reduction of water contamination and soil erosion (Day et al., 2005). Past studies assessed bio-char as combustion fuel to fire the pyrolysis system (Boatang et al., 2007), to treat tetracycline (TC) and chlortetracycline (CTC) used for growth promotion and therapeutic purposes in livestock production (Pils and Laird, 2007), and to provide energy for drying feedstock in combustors (Putsche, 2004).

Syngas is a co-product from biomass pyrolysis. It has been demonstrated in the combined heat and power (CHP) industry (Bain and Overend, 2002) that contains primarily H_2, CO, and CO_2. When converted to syn-fuel, it benefits the environment because syngas is sulfur free and contains oxygenates that result in less CO emissions and ozone to the atmosphere (Mills, 1994; Bain and Overend, 2002). Furthermore, through various technologies, fuels of widely varying compositions can be selectively synthesized that have high engine performance characteristics and energy efficiencies. Fischer-Tropsch synthesis (Chanenchuk et al., 1991; Bakkerud, 2005; Wilhelm et al., 2001) may be used to selectively convert syngas to high-molecular-weight hydrocarbons using catalysts (Lee, 1990; Catalytica, 1991; Unzelman, 1989). Depending on the pyrolysis gas composition and economics of the available catalysts, a pathway to liquid fuels can be selected.

There have been many studies of switchgrass bio-oil production by pyrolysis, including reactor design, and pyrolysis product characterization. However, few studies have fully characterized the pyrolysis process and the products resulting from pyrolysis at different temperatures. By characterizing the pyrolysis process and its products (bio-oil, syngas, and bio-char), the chemical composition and physical behavior of bio-oil can be better understood for further upgrading studies. The objectives of this switchgrass pyrolysis study were (1) to assess the effects of pyrolysis temperatures on the resulting bio-oil, syngas and bio-char production, (2) to characterize the products, and (3) determine the distribution of mass and energy of all the pyrolysis products.

3.2. Experimental

3.2.1. Biomass

Switchgrass samples provided by the Soil and Crop Sciences Department, Texas A&M University, were harvested in Pecos, Texas (Figure 3.1). Switchgrass feedstock was ground in a Wiley mill using a 2-mm screen. It had a moisture content of 8.4% prior to pyrolysis.

Fig. 3.1. Switchgrass plant (left) and lignocellulosic biomass used for pyrolysis (right).

3.2.2. Feedstock characterization

National Renewable Energy Laboratory (NREL) standard biomass analytical protocol was followed for structural compositional analysis (cellulose, hemicellulose, lignin, extractives). Proximate analysis; moisture Content (MC), volatile combustible matter (VCM), fixed carbon (FC) and ash were determined by ASTM D 3173, ASTM E 3175 and ASTM E 1755, respectively. Ultimate analysis (C, H, N, S, O) was performed using the Ultimate Analyzer Elementar, Vario Micro Cube, 15102013. Heating value

was determined using the bomb calorimeter, which includes the Parr 6200 Calorimeter, and Parr 6510 water-handling system.

3.2.3. Pyrolysis

Pyrolysis was performed in a Parr Instrument Co. pressure reactor (Figure 3.2). Prior to the pyrolysis runs, the reactor was purged with nitrogen and then filled with 360 g of switchgrass for all experiments. Pyrolysis was conducted at three temperatures; 400, 500 and 600 ^{0}C. Pressure in the reactor was kept constant at 7 bar (100 psig). The temperature of the reactor was raised at 6 ^{o}C (±0.3)/min to the final temperatures of pyrolysis (400, 500 and 600 ^{o}C), and this heating rate was consistent for all experiments. The reaction time was 20 (±3) min or until no significant gas release was observed. After 20-min retention time, the reactor was cooled to room temperature. The oil was condensed by a chiller and was collected for further analysis. Syngas was measured by water displacement and was collected during the reaction for compositional analyses. Bio-char was collected for mass and energy balance and was further analyzed. All experiments were performed in triplicate.

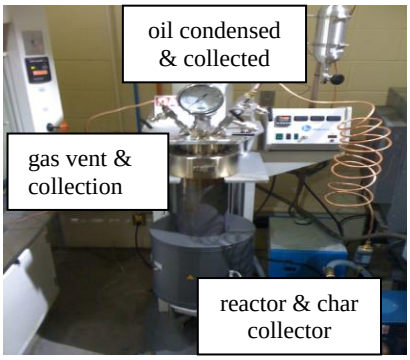


Fig. 3.2. Pyrolyzer used for experiments.

3.2.4. Product characterization

Bio-oil water content was determined by ASTM E 203 by Karl-Fischer (K-F) titration, (701 KF Titrino, Metrohm Brinkmann). Viscosity of the bio-oil was determined by ASTM D 445, using a kinematic viscosity bath, (Koehler Instrument Company, Inc.). GC/MS analysis of bio-oil was performed on a Shimadzu GCMS-QP2010 Plus equipped with an Agilent 5973 mass selective detector (MSD). The GC column used was a DB-WAX 122-7032, 30-cm long with 0.25-mm ID and 0.25-μm film. The oven was programmed to hold at 45 ^{o}C for 4 min, ramp at 3 ^{o}C /min to 280 ^{o}C and held for 20 min. The injector temperature was 250 ^{o}C, and the injector split ratio was set at 30:1. Carrier gas helium flow rate was 1 mL/min. The bio-oil samples were prepared as 10% solution in chloroform. For quantification of components, relative response factors were determined relative to the internal standard (Oasmaa and Meier, 2005). Proximate and ultimate analyses and heating value of bio-oil were determined using the protocol stated above under feedstock characterization.

Syngas samples were collected at the different pyrolysis temperatures and were analyzed on the SRI 8610 C gas chromatograph. The columns for the syngas analyses were molecular sieve 13x and shin carbon ST. The detector for H_2 gas was helium ionization detector (HID) and for all other syngas components was thermal conductivity detector (TCD). The oven was programmed to hold at 55 ^{o}C for 8 min, ramp at 20 ^{o}C/min up to 250 ^{o}C, and hold for 15 min. Both detectors were maintained at 150 ^{o}C. A mixture of standard gases (H_2, CO, CO_2, CH_4, C_2H_4) was used as the internal standard

for quantification. The heating values from gas compositional analyses were then calculated based on higher heating values of CO, H_2, CO_2, CH_4, C_2H_4, C_2H_6.

Bio-chars from different pyrolysis temperatures were tested for their heating values and for proximate and ultimate analyses using the protocol stated under feedstock characterization. Bio-char surface area and pore volume were measured using the Brunauer-Emmett-Teller (BET) analyzer on a Nova 4200e, (Quantachrome Instrument) in an automated volumetric nitrogen adsorption apparatus at 77 K. Bio-char samples were degassed at 300 ^{o}C for 12 hours before adsorption measurements.

3.2.5. Energy balance calculation

Energy input in to the pyrolysis system was calculated based on the biomass energy (8,524 Btu/lb, Section 3.2.2 for heating value) and the heat energy calculated (3.42 Btu/s) supplied to the system. Energy output was the total energy from bio-oil, syngas and bio-char (Section 3.2.2 for heating value/energy content calculations). Further, the energy loss in the system was total energy output subtracted from total energy input.

3.3 Results and discussion

3.3.1. Characterization of feedstock

Table 3.1 presents physical, elemental and structural analyses of the feedstock (switchgrass) used for all pyrolysis runs. These data were comparable to those of Boateng et al. (2007) and Adler et al. (2006). Depolymerization and fragmentation of cellulose, hemicellulose, and lignin form a multi-component bio-oil mixture; thus, structural composition is important (Zhang et al., 2007). Alkali metals contained in ash

may catalyze the depolymerization mechanisms during pyrolysis, resulting in changes in the composition of pyrolysis products (Fahmi et al., 2007). However, in this case, we did not consider such catalytic behavior because ash content was only 3.9%, and volatile content was high (84%) (Table 1). Low nitrogen content implies very low protein content in switchgrass. The heating value of switchgrass was 8,524 Btu/lb or 19.8 MJ/kg.

Table 3.1
Proximate, ultimate and structural analyses of biomass samples used for pyrolysis.

Proximate	Switchgrass (wt%)	Ultimate	Switchgrass (wt%)	Structural	Switchgrass (wt%)
Moisture	8.4	C	42	Cellulose	32
Volatile matter	84.2	H	6.1	Hemicellulose	19.2
Ash	3.9	N	0.4	Lignin	18.8
Fixed carbon	11.9	S	0.1	Extractives	18.5
		O	47.4		

3.3.2. Effects of pyrolysis temperature on products yields

Bio-oil, syngas and bio-char yields were determined at three pyrolysis temperatures; 400, 500 and 600 ^{o}C (Figure 3.3). With increase of the pyrolysis temperature, bio-oil and syngas yields increased, whereas bio-char yield decreased. Pyrolysis at 400 ^{o}C yielded 22% bio-oil and 8% syngas, whereas pyrolysis at 600 ^{o}C yielded 37% bio-oil and 26% syngas. Bio-char yield decreased from 48% at 400 ^{o}C to 25% at 600 ^{o}C (Figure 3.3). Pyrolysis products from oil seeds of other plants determined at different temperatures had trends similar to those obtained in this research (Onay, 2007). Yang et al. (2005) categorized pyrolysis in a four-stage process with the following steps; moisture evolution (<220 ^{0}C), hemicellulose decomposition (220−315

°C), cellulose decomposition (315−400 °C), and lignin degradation (>400 °C). Higher temperature of pyrolysis results in higher heating rate and higher lignin degradation that may result in higher oil production (Onay et al., 2007; Yang et al., 2005). On the other hand, increase in gaseous products at higher pyrolysis temperature of 600 °C is caused by secondary cracking of the pyrolysis vapors and secondary decomposition of the bio-char (Onay, 2007). A similar trend in gas production was reported in other studies (Luo et al., 2004; Horne and Williams, 1996). For optimum production of switchgrass bio-oil and upgrading processes, we will pyrolyze samples at 600 °C in future research.

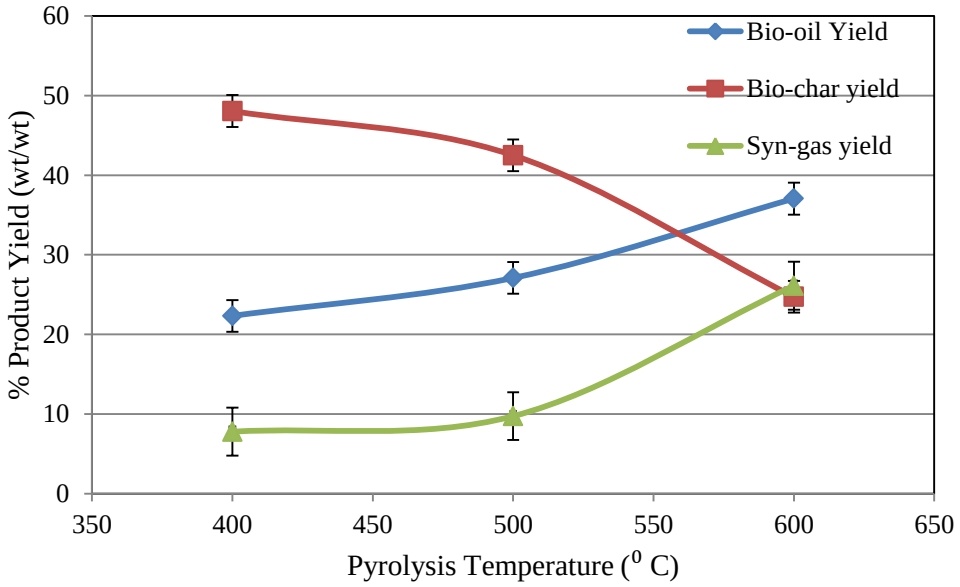


Fig. 3.3. Products; bio-oil, syngas and bio-char yields from switchgrass as a function of pyrolysis temperature.

3.3.3. Bio-oil characterization

Properties of the bio-oil are affected by feedstock variation, production processes, reaction conditions, and collecting efficiency. Elemental analysis and properties of bio-oil from switchgrass pyrolysis at 600 ^{o}C are compared with gasoline and diesel (Table 3.2). The bio-oil was highly oxygenated (37%), which is consistent with results of other studies that show a range of 35−40% oxygen in bio-oil (Oasmaa and Meier, 2005; Scholze and Meier, 2001). Oxygen is distributed among various compounds, depending on the resource of biomass and conditions of pyrolysis. Presence of oxygen results in lower energy density, high acidity, and immiscibility with hydrocarbon fuels (Zhang et al., 2007). Moisture content of the bio-oil was 13%, resulting from the original feedstock moisture and the dehydration products of during pyrolysis reactions (Shihadeh and Hochgreb, 2002). NREL (National Renewable Energy Laboratory) studies showed that additional thermal cracking of bio-oil improved its chemical and vaporization characteristics, resulting in lower water content and lower molecular weight (Zhang et al., 2007; Shihadeh and Hochgreb, 2002). The viscosity of our bio-oil is 10 cSt, which is comparatively higher than viscosities of gasoline or diesel (Table 3.2). Studies of bio-oil viscosity showed that viscosity is lowered by high water content, low water insolubles, and alcohol presence/addition (Sipilae et al., 1998; Boucher et al., 2000). Heating value of the bio-oil obtained in this experiment is 36.3 MJ/kg, or 15,600 Btu/lb.

Table 3.2
Ultimate analysis and physical properties of switchgrass bio-oil.

Ultimate Analysis	Bio-oil (%)	*Gasoline (%)	*Diesel (%)	Properties	Bio-oil	Gasoline	Diesel
C	50	84.5	86.6	Heating value (MJ/kg)	36.3	47.3	45.5
H	9.3	13.1	13.3	Moisture content (%)	13	<0.1	<0.1
N	1.5	–	0.0065	Density (kg/m^3)	920	723	838
S	0.6	<0.0001	0.11	Viscosity (cSt)	10	0.12	2.1
O	37	2-6	1.8				

*Gasoline source: (Galiasso et al., 2008), *Diesel source: (Miao et al., 2004; Yusuf, 1995)

Composition of the bio-oil from switchgrass pyrolysis is presented as whole bio-oil that has an aqueous phase (Figure 3.4). Distributions of the aqueous phase, bio-oil phase and the total of the two phases show that at 400 ^{o}C, 4% of the whole bio-oil was oil phase and 19% was aqueous phase (Imam and Capareda, 2011). The percentage of the oil phase increased with pyrolysis temperature to 7% at 500 ^{o}C and 12% for 600 ^{o}C. The aqueous phase also increased to 20% and 25% for 500 and 600 ^{o}C pyrolysis, respectively. Because of the difference in density of the aqueous phase (1100 kg/m^3) and oil phase (920 kg/m^3), the two phases are easily separated. Compositions are used to categorize the oil phases as alkanes (Table 3.3), phenols (Table 3.4), aromatics; indene, methyl-indene, benzene, toluene, methyl-napthalene (Table 3.5), and esters, acids, alcohols, ketones and other components (Table 3.6). Chemical composition of the aqueous phase of the bio-oil is further presented in Table 3.7.

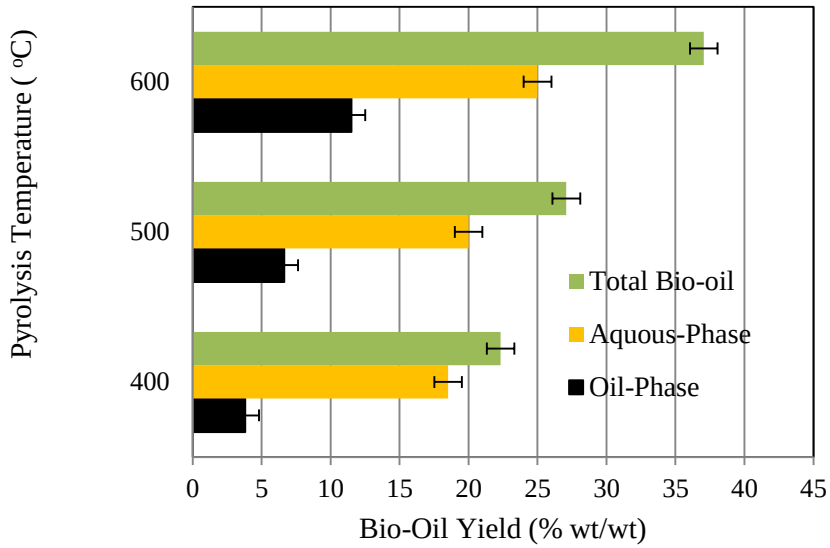


Fig. 3.4. Percentage of bio-oil and its aqueous phase from switchgrass at different pyrolysis temperatures.

Table 3.3
Branched hydrocarbon; alkanes detected in switchgrass pyrolysis oil.

Compound	(%)	Total (%)
Dodecane	7.3	
Undecane, 2,6-dimethyl-	1.3	
Octane, 3,6-dimethyl-	2.9	
Tridecane	2.6	
Dodecane, 2,5-dimethyl-	0.6	
Hexadecane, 1-bromo-	1.4	
Tridecane, 4-methyl-	0.3	
Decane, 3,8-dimethyl-	0.4	
Dodecane, 2,6,10-trimethyl-	3.5	
Cyclotetradecane	1.3	
Cyclododecane	0.3	
Dodecane, 4,6-dimethyl-	1.8	
Tridecane, 2-methyl-	0.5	
Decane, 1-bromo-2-methyl-	0.3	
Hexane, 2-phenyl-3-propyl-	0.2	
Hexadecane	8.5	
Octadecane	0.3	
Heptadecane	2.6	36.2

Table 3.4
Phenolic compounds detected in switchgrass pyrolysis oil.

Compound	(%)	Total (%)
Phenol, 2-ethyl-	1.5	
Phenol, 4-ethyl-	3.3	
Phenol, 3,5-dimethyl-	1.4	
2-methoxy-5-methylphenol	0.4	
Phenol, 2-1-methylethyl- acetate	1.2	
Phenol, 2,4,5-trimethyl-	1.3	
Phenol, 4-propyl-	0.6	
Phenol, 4-ethyl-2-methoxy-	6.4	
Phenol, 5-methyl-2- acetate	1.1	
Phenol, 2,6-dimethoxy-	0.9	
Phenol, 2-methoxy-4-methyl-	2.3	20.5

Table 3.5
Aromatics; indene, benzene, napthalene, and toluene detected in pyrolysis oil.

Compound	Group	(%)	Total (%)
1h-indene, 2,3-dihydro-4,7-dimethyl-	Aromatics	0.3	11
1h-indene, 2,3-dihydro-1,1,5,6-tetramethyl-		0.4	
1-tetradecene		3.1	
3-octadecene, (e)-		0.4	
1-heptadecene		0.8	
9-eicosene, (e)-		0.3	
2-hexadecene, 3,7,11,15-tetramethyl		0.2	
1-decene, 3,3,4-trimethyl-		0.5	
2,4-diphenyl-4-methyl-1-pentene		0.2	
5,8-dimethylenebicyclo[2.2.2]oct-2-ene		0.7	
1,4-dihydronaphthalene		0.5	
Benzene, 1-ethyl-3-methyl-		2.2	
5-octadecene, (e)-		1.2	
Naphthalene, 2-methyl-	Napthalene	0.7	1.7
Naphthalene, 1,2,3,4-tetrahydro-5,6,7,8-tetramethyl-		0.4	
Naphthalene, 1,5-dimethyl-		0.6	
Toluene, 4-(1,1-dimethyl-2-propynyloxy)-	Toluene	0.3	1.4
1,1'-bicyclohexyl		0.6	
Fluorene, 2,4a-dihydro-		0.5	

Table 3.6
Furans, ketones, acids, alcohols, ester and amide detected in switchgrass pyrolysis oil.

Compound	Group	(%)	Total (%)
Furfural	Furan	0.8	4.2
2-hexanoylfuran		1.3	
Benzofuran, 4,7-dimethyl-		1.7	
Benzofuran, 2-methyl-		0.5	
Cyclopentanone, 2-methyl-	Ketone	1.8	5.1
1-(3h-imidazol-4-yl)-ethanone		0.6	
Ethanone, 1-[4-(1-methylethenyl)phenyl]-		1.1	
Cyclohexanone, 4-(benzoyloxy)-		0.3	
2-tridecanone		0.7	
2-pentadecanone, 6,10,14-trimethyl-		0.4	
Cyclopentanone, 2-ethyl-		0.2	
Benzoic acid, 4-isopropenylcyclohexenylmethyl ester	Fame/acid	0.9	8.7
9-hexadecenoic acid, methyl ester, (z)-		0.4	
Pentadecanoic acid, 14-methyl-, methyl ester		1.1	
Pentadecanoic acid		0.6	
Oxalic acid, 2-isopropylphenyl pentyl ester		2.0	
Oxalic acid, isobutyl 2-isopropylphenyl ester		1.7	
Oxalic acid, 6-ethyloct-3-yl ethyl ester		1.2	
Dodecanoic acid, methyl ester		0.5	
Acetic acid, trichloro-, nonyl ester		0.3	
Mequinol	Alcohol	0.4	7.4
Thymol		1.0	
Benzenepropanol, 2-methoxy-		0.8	
1-dodecanol, 3,7,11-trimethyl-		2.9	
3,7,11,15-tetramethyl-2-hexadecen-1-ol		0.3	
1h-benzimidazole, 5,6-dimethyl-		0.8	
Benzeneethanol, .alpha.-methyl-		0.7	
3-buten-2-ol, 4-phenyl-		0.5	
Isodecyl methacrylate	Ester	1.9	2.4
Methyl n-isopropyl-3-phenylpropanimidate		0.6	
Acetamide, 2-(1-naphthyl)-n-(3,4-methylendioxybenzyl)-	Amide	1.5	1.5

Table 3.7
Compounds detected in aqueous phase of bio-oil from switchgrass pyrolysis.

Compounds	Group	(%)
2-propanone	Ketone	13
Acetic acid, methyl ester	Ester	8.1
2,3-butanedione	Ketone	2.8
2-butanone	Ketone	17
Furan, tetrahydro-	Furan	4.5
2-pentanone	Ketone	3
Acetic acid	Acid	28
2-propanone,	Ketone	1.8
Cyclopentanone	Ketone	2.6
2-furancarboxaldehyde	Aldehyde	6.6
Cyclopentanone, 2-methyl-	Ketone	1.5
2-cyclopenten-1-one, 2-methyl-	Ketone	1.6
5-decene	Alkene	1.1
Cyclopentane, 1,1,3-trimethyl-	Alkane	1.3
4-nonene, 5-methyl-	Alkene	1.0
1-decene	Alkene	1.1
Phenol, 2-methyl-	Phenol	1.5
Phenol, 2-methoxy-	Phenol	3.2

Bio-oil from switchgrass is composed of a complex mixture of alcohols, esters, ketones, lignin-derived phenols, long-chain alkanes, aldehydes, fatty acid methyl esters, furans, napthalene, amides, and various aromatics (Tables 3.3−3.6). The GC-MS analysis of the switchgrass bio-oil from this research shows that its composition is similar to switchgrass bio-oil analyzed by Guo et al., (2001). Many of the components identified are phenols and long-chain hydrocarbons, and most functional groups show presence of oxygen. Analyses of bio-oil and the aqueous phase are grouped into various hydrocarbon groups to clarify chemical properties and to upgrade products for future research. The results show 36% branched and long-chains alkanes (Table 3.3); 20% methyl, methoxy and propenyl attached phenols (Table 3.4); 14.1% aromatics (indene,

methyl-indene, benzene, toluene, methyl-napthalene, Table 3.5); 8.7% mixed acids and methyl ester fatty acids (Table 3.6); 7.4% methyl, methoxy attached alcohols (Table 3.6); and the rest mostly are furans and ketones. The complex mixture of switchgrass bio-oil from this research is comparable to that of Peng and Wu's (2000) study of bio-oil.

Table 3.7 shows the distribution of some detected compounds in the aqueous phase of the bio-oil from switchgrass pyrolysis. This aqueous phase is comprised mainly of acetic acid (28.2%) and various branched ketones (42%), small amounts methyl and methoxy phenols (4.7%), and minor aromatic hydrocarbons. Presence of abundant aldehydes and ketones (Table 3.7) make this aqueous phase of the oil hydrophilic (Zhang et al., 2007) and highly hydrated, which makes it difficult to eliminate water from the bio-oil.

3.3.4. Syngas characterization

Total produced syngas increased from 8% at pyrolysis temperature of 400 ^{o}C to 26% at pyrolysis temperature of 600 ^{o}C (Figure 3.3). Syngas composition varied with pyrolysis temperature (Table 3.8). With an increase in temperature, CO_2, CO, C_2H_4, and C_2H_6 contents increased, whereas H_2 and CH_4 contents decreased. Similar trends for CO and CO_2 were shown by Baker et al. (2005), where the increase in CO and CO_2 was explained by the oxidation of the carbonized bio-char at higher temperatures of pyrolysis (Lee and Fasina, 2009; Baker et al., 2005). In their study, other components of the syngas had no significant variations in abundance with increasing pyrolysis temperature (Baker et al., 2005).

Table 3.8
Syngas composition as a function of pyrolysis temperature.

Pyrolysis *T* (^{0}C)	H_2 (%)	CO (%)	CH_4 (%)	CO_2 (%)	C_2H_4 (%)	C_2H_6 (%)
400	28.0	21.7	39.2	9.1	1.2	0.8
500	25.4	21.5	39.4	9.4	2.3	1.9
600	9.7	27.7	17.6	33.2	4.3	7.0

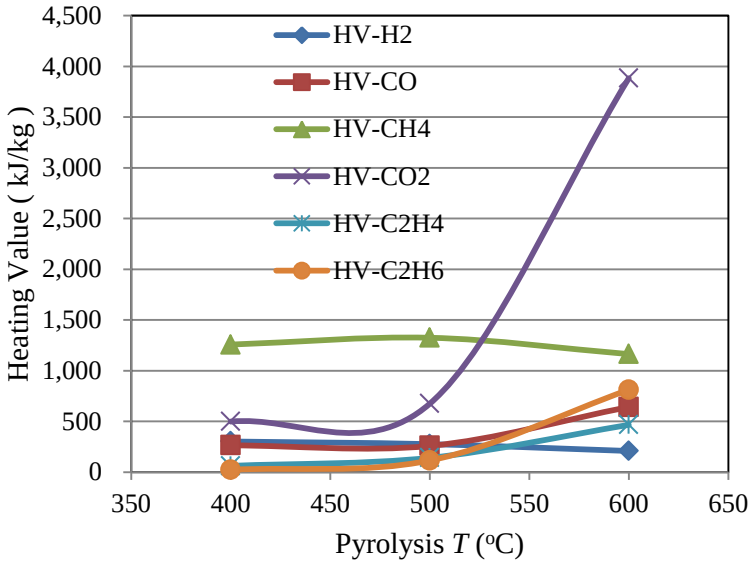


Fig. 3.5. Heating value of syngas as a function of pyrolysis temperature.

Syngas heating values were analyzed based on the standard heating values from combustion of common fuel gases reported in the Engineering Handbook (http://www.engineeringtoolbox.com/heating-values-fuel-gases-d_823.html). The heating values of our gas samples varied with gas compositions that, in turn, resulted from different pyrolysis temperatures. Heating values of gases increased as the contents of C_2H_6, CO, and C_2H_4 increased (Figure 3.5). There was a decrease in CH_4 and H_2 production with increasing pyrolysis temperature (Table 3.8), causing decrease in the

heating values from these gases. At the higher temperature of 600 ^{o}C, more C and CO were oxidized to CO_2, causing the C to CO_2 conversion heating value to increase relative to the lower temperatures of 400 and 500 ^{o}C. This is shown by higher CO_2 production at 600 ^{o}C compared to 400 and 500 ^{o}C (Table 3.8).

3.3.5. Bio-char characterization

Bio-char yield from switchgrass pyrolysis decreased from 48% to 43% from samples pyrolyzed at 400 and 500 ^{o}C, respectively; the bio-char yield decreased markedly from 43% to 25% between samples pyrolyzed at 500 and 600 ^{o}C, respectively (Figure 3.3). Proximate analyses of bio-chars from different pyrolysis temperatures are characterized in Figure 3.6, and ultimate analyses of bio-char are presented in Table 3.9. The volatile content of bio-char decreases from 20% to 17.8% for samples pyrolyzed at 400 and 500 ^{o}C, respectively; volatile content further decreases to 8.2% for samples pyrolyzed at 600 ^{o}C. Fixed carbon content is approximately 70% for samples pyrolyzed at 400 and 500 ^{o}C, but it increases to 79% for samples pyrolyzed at 600 ^{o}C. Ash content increases slightly with increasing pyrolysis temperature (Figure 3.6). This can be explained by higher pyrolysis temperature removing greater percentages of volatiles.

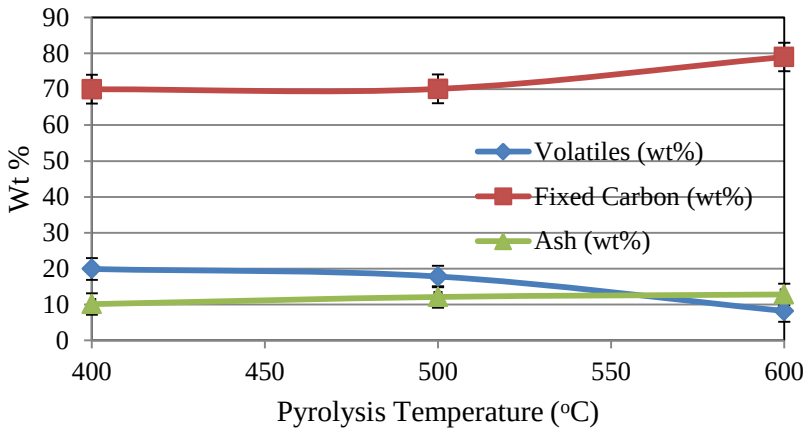


Fig. 3.6. Proximate analyses of bio-char at various pyrolysis temperatures.

Char elemental analysis shows that carbon content increased, whereas oxygen and hydrogen contents decreased with increasing pyrolysis temperature (Table 3.9). A similar trend was reported by Onay (2007). Losses in hydrogen and oxygen are explained by breaking of weaker bonds within the bio-char structure and the bio-char becoming highly carbonaceous at higher pyrolysis temperatures (Onay, 2007; Cai et al., 1996). The heating values of bio-char increased slightly with an increase in pyrolysis temperature (Table 3.9). This may be caused by the slight increase in the carbon content in bio-char with increased temperature.

Table 3.9
Elemental composition, heating value, surface area and total pore volume of bio-char.

Pyrolysis *T* (°C)	C (%)	H (%)	N (%)	O (%)	S (%)	HV (MJ/kg)	Surface area (m^2/g)	Pore volume (cm^3/g)
400	75.2	4.9	1.9	17.7	0.3	28.9	0.1	0.6
500	78.3	3.6	1.3	16.5	0.3	29.0	0.9	0.7
600	82	2.4	1.2	14.1	0.3	29.4	1.0	0.7

The reactivity and combustion behavior of bio-char are strongly affected by surface area (Onay, 2007). With an increasing pyrolysis temperature from 400 to 600 ^{0}C, the surface area of the char increases from 0.1 to 1.0 m^2/g (Table 3.9). Higher pyrolysis temperature causes higher devolatilization, resulting in more pore volume in the samples and, in turn, greater surface area for reaction or adsorption activities (Zanzi et al., 2002). The total pore volume per gram of sample also increases with temperature (Table 3.9). These trends of increased porosity and surface area with increased pyrolysis temperature are consistent with results reported in other studies (Zanzi et al., 2002; Guero et al., 2005; Cetin et al., 2005).

3.3.6. Pyrolysis products mass balance and energy distribution

Product distributions differ with pyrolysis temperatures (Figure 3.7). Product recovery increases (loss is less) with increasing temperature: 88% at 600 ^{o}C; 80% at 500 ^{o}C; and 78% at 400 ^{o}C. The mass loss may have been from the non-condensable gases or from incomplete bio-oil recovery during collection. The percentages of produced bio-oil and syngas increase with higher pyrolysis temperature, at the expense of bio-char (Figure 3.7). Agblevor et al. (1996) showed 7.4% mass loss for fluidized bed pyrolysis of switchgrass, and Mullen et al. (2010) reported 19 to 26% mass loss, where the loss was mostly unused biomass remaining in the tubing and piping of the pyrolyzer. In comparison, in this study, mass loss varied from 12−22%. Lee and Fasina, (2009) further explained a low heating rate (10 ^{o}C/min), which is close to the heating rate of this research (6 ^{o}C/min), resulted in lower mass loss compared to higher heating rates of more than 10 ^{o}C/min.

Figure 3.8 shows the energy distribution of the pyrolysis products and energy losses in the system at different pyrolysis temperatures. Energy loss was the lowest at the highest temperature (600 ^{o}C), which may be caused by the higher energy value from the greater amount of bio-oil and syngas production in comparison to the pyrolysis at lower temperatures (400 and 500 ^{o}C). The energy value of the produced syngas increases from 11 to 13% and finally to 28% with increasing pyrolysis temperature (Figure 3.8). Because bio-oil production increases significantly with pyrolysis temperature, the energy content of bio-oil at 600 ^{o}C is significantly higher (47%) in comparison to energy content for oils from switchgrass pyrolyzed at 400 and 500 ^{o}C (33% and 39%, respectively). Mullen et al. (2010) showed energy loss of 25%, which was explained as reactor heat loss and energy lost from the condenser, whereas Boateng et al. (2007) reported 18% energy loss from heat losses from the input energy.

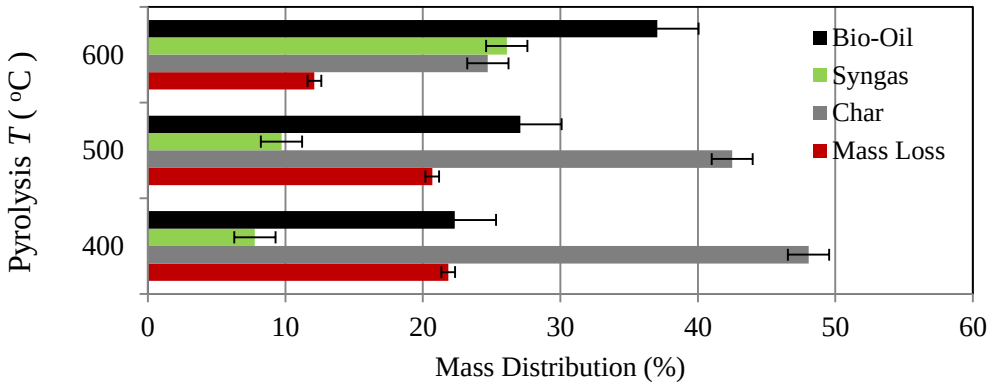


Fig. 3.7. Product distribution for different pyrolysis temperatures.

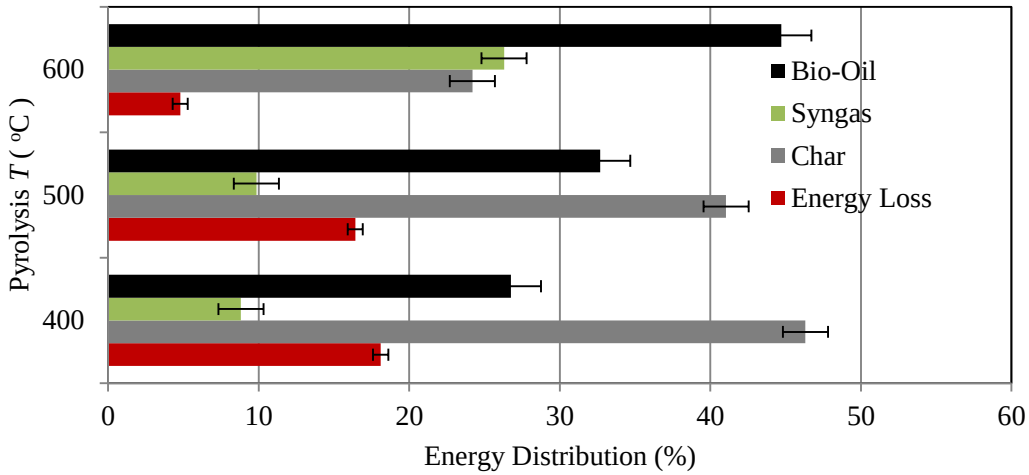


Fig. 3.8. Energy distribution for different pyrolysis temperatures.

3.4. Conclusions

Bio-oil and syngas yields increase, whereas bio-char yield decreases with increasing temperature of pyrolysis. From pyrolysis at 600 °C, product yield was 37% bio-oil, 26% syngas and 25% bio-char. However, at 400 °C, product yield was 22% bio-oil, 8% syngas and 56% bio-char. Efficiency of pyrolysis improved with the pyrolysis temperature; product yield increased from 78% at 400 °C to 88% at 600 °C.

The bio-oil was highly oxygenated (37 wt%). It had a heating value of 36.3 MJ/kg. Viscosity of the bio-oil was 10 cSt, which is comparatively higher than viscosities of gasoline (0.12) or diesel (2.1). The oil phase is a complex mixture of hydrocarbons (alkanes, phenols, aromatics, acids, alcohols, and ketones), and the aqueous phase is comprised mainly of branched ketones and acetic acid. For syngas, heating values of CO, C_2H_4, C_2H_6, and C to CO_2 conversion increase, whereas heating values of H_2 and CH_4 decrease at higher temperature, owing to decrease in the volumes

of the latter products. This is caused by the compositional variations of the syngas components; CH_4, and H_2 production decreases whereas CO, CO_2, C_2H_4 and C_2H_6 production increases with pyrolysis temperature. The fixed carbon increased and volatile matter content of bio-char decreased with increasing temperature of pyrolysis. Bio-char surface area increased from 0.1 m^2/g at 400 ^0C to 1.0 m^2/g at 600 ^oC pyrolysis.

From pyrolysis at 400 ^oC, energy distribution was 33% from bio-oil, 11% from syngas, and 56% from bio-char. From pyrolysis at 600 ^oC, energy distribution was 47% from bio-oil, 28% from syngas, and 25% from bio-char. Because bio-oil and syngas yields are significantly greater from switchgrass pyrolysis at high temperature, future research will pyrolyze samples at 600 ^oC to optimize production of bio-oil and to upgrading pyrolysis processes.

This research advances understanding of products and mass balance from pyrolysis of switchgrass, a renewable energy source that is readily available globally. Bio-oil, syngas, and bio-char are important pyrolysis products in terms of energy supply and the environment concerns. Biomass may be considered a viable, renewable energy source when used in an integrated process where all three pyrolysis products are marketed to maintain sustainable development and improve project economics. In the next chapter, bio-oil produced in this research will be upgraded to transportation fuel.

4. DESIGN AND DEVELOPMENT OF CATALYTIC HYDROGENATION TECHNOLOGY TO UPGRADE PYROLYSIS OIL TO GASOLINE

4.1 Introduction

Upgrading bio-oil to transportation fuel requires chemical transformation of the oil to increase its volatility and thermal stability, and to reduce viscosity by removing objectionable oxygen. A crucial difference between bio-oil and crude oil (<1% O_2) is that bio-oil contains 10−40% oxygen (Zhang et al., 2007; Venderbosch and Prins, 2010), which affects homogeneity, polarity, heating value, and acidity of the oil (Mullen et al., 2010). Such characteristics of the bio-oil cause instability during storage, and thus, bio-oils are easily oxidized (Oasmaa and Kuoppala, 2003). Various technologies are under development and may play a significant role in future production of biofuels to replace increasingly expensive petroleum. Two main processes used to reduce the oxygen content and upgrade bio-oil for use as a transportation fuel follow: (1) bio-oil catalytic cracking, or catalytic cracking in combination with catalyst fast pyrolysis; and (2) hydrodeoxygenation (HDO). The product of zeolite cracking of bio-oil contains 13−24 wt% oxygen. In contrast, the product of HDO technology contains <5 wt% oxygen.

The main limitations of zeolite catalytic cracking are high coking (8−25 wt%), poor fuel quality, and rapid deactivation of catalysts. In studies of pore blockage, HZSM-5 showed low reactivity with high-molecular-weight aromatics and resulted in rapid zeolite deactivation (Guo et al., 2009). During catalytic cracking, acid sites on zeolites significantly influence the carbon-forming reactions. Studies report proton donation as a source of hydrocarbon cations, and during cracking, catalysts led to poly

(aromatic) carbon species because of its hydrogen-deficient nature (Huang et al., 2009). Also, studies indicate zeolite regeneration may not be an efficient possibility because, after five regeneration cycles, the oxygen content of the catalytic upgraded product increased from 21 to 30 wt% (Guo et al., 2004). On the other hand, primary HDO limitations are high-pressure hydrogen requirement and optimization for industrial-scale production, in addition to deactivation of catalysts. During HDO, the following factors cause catalyst deactivation: (1) Carbon formation during polymerization based on feed composition and process conditions (Wildschut, 2009; Fonseca et al., 1999), and (2) increase in catalyst acidity resulting in coking (Wildschut, 2009; Richardson et al., 1995). Various processes need to be improved before HDO or zeolite cracking can be used on an industrial scale. These include the following; decrease in process temperature, decrease in hydrogen usage and sustainable sources for the hydrogen use, improve carbon formation during bio-oil upgrade, improve catalyst development and lifetime, understand kinetics of HDO of bio-oil or model compounds, lower the degree of deoxygenation in the final product, and reduce influence of bio-oil impurities on catalysts.

The objective of this study is to develop a novel technology and build a continuous system to upgrade pyrolysis bio-oil for use as transportation fuel. This new technology focused on the following: (1) converting objectionable oxygenates (peroxide, aldehyde, ketone, carboxylic acid) to stable oxygenates, like alcohol, for a stable fuel; (2) convert any di/tri olefins to mono-olefins to reduce gum problem; and (3) hydrogenate reactive and unstable compounds like styrene to ethyl benzene or

cyclohexane, indene to indane, and poly-aromatics to mono-aromatics, respectively. This is unlike previous studies that mostly focused on removing oxygen.

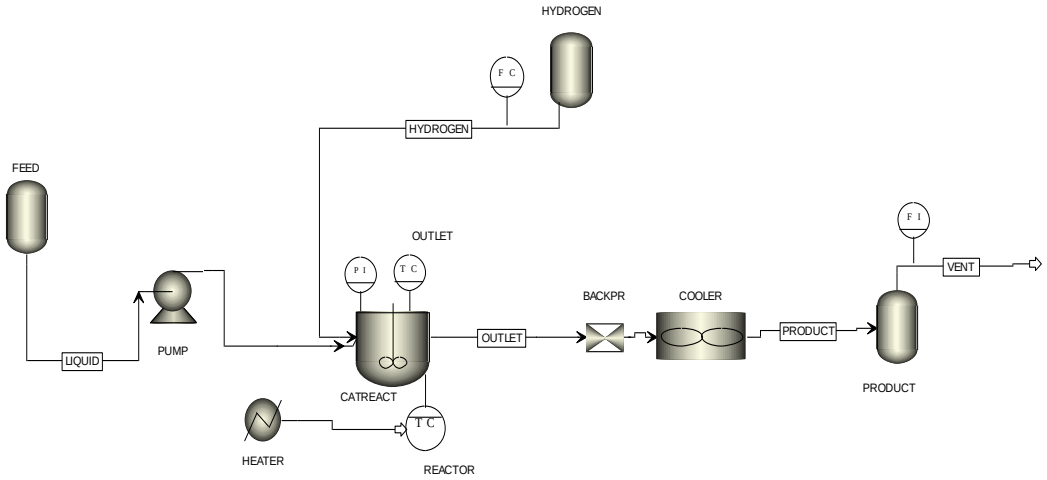
4.2 Experimental

4.2.1 Feed and product characterization

The water content in bio-oil, its light fraction, and upgraded product (switchgrass, (SG) gasoline) was determined by ASTM E 203 by Karl-Fischer (K-F) titration, (701 KF Titrino, Metrohm Brinkmann). Viscosity was determined by ASTM D 445, using Kinematic Viscosity Bath, (Koehler Instrument Company, Inc.). Ultimate analysis (C, H, N, S, O) was performed using the Ultimate Analyzer Elementar (Vario Micro Cube, 15102013). Heating value was determined using a bomb calorimeter (Parr 6200 Calorimeter and Parr 6510 water handling system).

4.2.2 Design of the bio-oil upgrading system

A bio-oil upgrading system (Figure 4.1) was designed, built, and tested to convert bio-oil to gasoline-like fuel. The upgrade apparatus consisted of a catalytic reactor (Autoclave Engineers), HPLC pump (Scientific Systems) for feed transport, mass flow controller (Aalborg) for hydrogen gas flow, motor speed and heater controller with readout systems (Autoclave Engineers) for controlling temperature and stirring speed during the experiment, system lines of stainless steel, back pressure regulator, and proportional relief valve (Swagelock). The size of the reactor or catalyst basket was 7.1 mL with a free volume of 50 mL (Autoclave Engineers).



FC – Flow controller FI – flow indicator PI – Pressure indicator TC – Temp Controller BACKPR – Back pressure regulator

Fig. 4.1. Bio-oil upgrade system design.

4.2.3 Catalyst specifications and activation process

The nickel catalyst (HTC NI 200 RPS 2.5 mm) was supplied in reduced and air-passivated form and was treated with an organic sulphiding agent by Johnson Matthey Catalysts. The specifications of the catalyst are presented in Table 4.1.

Table 4.1
Physical properties and chemical composition of the catalysts for bio-oil upgrade.

Physical properties	Sulfided nickel	Chemical composition	Wt% (dry)
Nominal size (mm)	2.5	Ni	>11.2%
BET surface area (m/g^2)	110	Organic S	1 to 3%
Pore volume (mL)	0.43	Alumina	Balance
Compacted bulk density (kg/m^3)	800		
Mean particle length (mm)	2.84		
Mean particle crush strength (N/mm)	24		
Loss on abrasion (wt%)	1.0		
Fines content (wt%)	<1.0		

Before use, the catalyst was activated to remove the oxide layer and to fix the sulphiding compound. For the activation process, the reactor was purged with nitrogen at 4.1 bar (60 psig). The system was tested for pressure leaks and was de-pressurized. The system was then pressurized with hydrogen at the lowest possible system pressure of 1−5 bar (14.5−72.5 psig). Hydrogen flow rate of 13 mL/min was established and maintained. The system was heated to 120 °C at a rate of 40 °C/h and temperatures was held constant for 12 h. At this temperature and hydrogen flow rate, the catalyst was activated for a period of 12 hours. After activation, the system was cooled to start the run temperature and pressurize to the operating pressure. For the upgrade experiment, hydrogen flow rate was adjusted to the required hydrogen oil ratio. The feed was then introduced to start a run.

4.2.4 Test specifications and protocol

Figure 4.2 summarizes the bio-oil upgrade. Bio-oil from switchgrass pyrolysis was distilled by ASTM D1160-06. The fraction below 140 °C (light fraction) was collected and any water was separated out of the fraction from the two phases. A true boiling point curve was generated from the distillation of the bio-oil. This bio-oil light-fraction was then upgraded on the catalytic reactor through a continuous run. The catalyst basket was packed with 3 g of catalyst with a weight hourly space velocity of (mass flow rate of feed/mass of catalyst), 8.75/h. After activating the catalyst, the hydrogen pressure was increased to 32.5 bar (470 psig) with a flow rate of 15 mL/min. Temperature was maintained at 110 °C and 120 °C for different runs. Once the hydrogen flow rate was stable, feed (bio-oil light fraction) flow was introduced at 0.5 mL/min.

This was run continuously for 12 h at a steady state and product was collected for analysis.

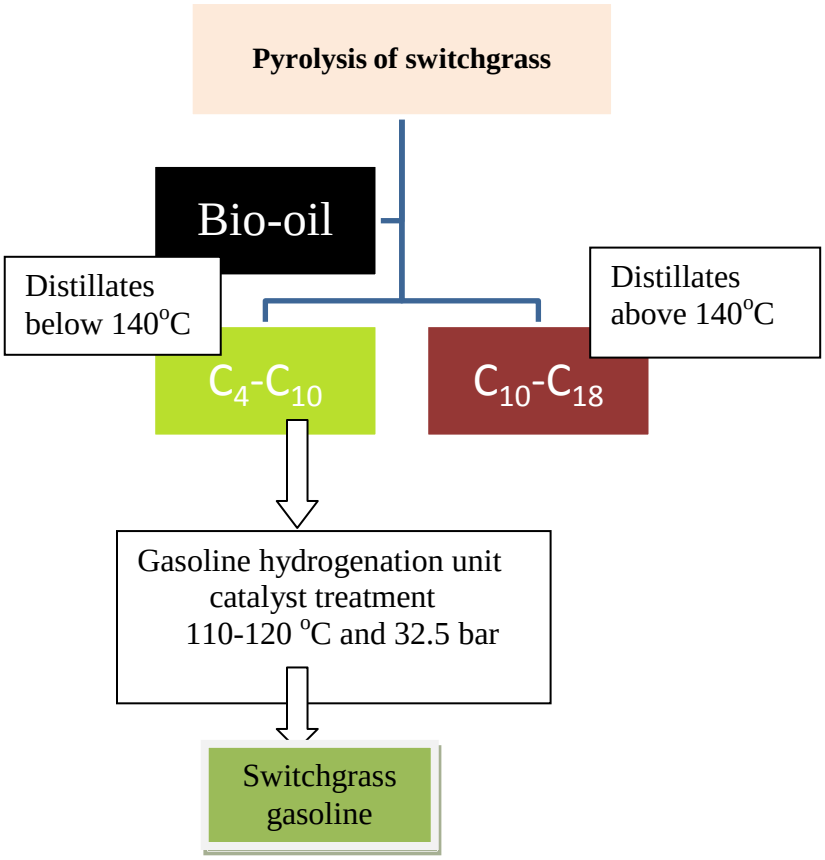


Fig. 4.2. Thermally converted biomass to bio-oil and its upgrade to gasoline through catalytic hydrogenation.

4.2.5 Analytical methods

GC/MS analysis of bio-oil, bio-oil light fraction, and upgraded product (SG gasoline) was performed on a Shimadzu GCMS-QP2010 Plus equipped with an Agilent 5973 mass selective detector (MSD). The GC column used was a DB-WAX 122-7032, 30-cm long with 0.25-mm ID and 0.25-µm film. The oven was programmed to hold at 45 °C for 4 min, ramp at 3 °C /min to 280 °C and hold there for 20 min. The injector

temperature was 250 ^{o}C, and the injector split ratio was set at 30:1. Carrier gas helium flow rate was 1 mL/min. The bio-oil samples were prepared as 10% solution in chloroform. For quantification of components, relative response factors were determined relative to the internal standard (Oasmaa and Meier, 2005). Thermal stability of the upgraded product was performed using D 525 and compared to typical gasoline stability (Southwest Research Institute (SwRI), San Antonio, TX).

4.2.6 Energy and cost calculation specifications

Input energy was calculated from the following; (1) the heater, which was on 30% of the time of the experiment, as dictated by the automatic controller; (2) magnetic stirrer, which was set at 18% (0.3) for its energy use for constant rotation of 300 revolutions per min; (3) pump; (4) liquid feed of 0.5 mL/min; (5) hydrogen flow of (15 mL/min); and (6) mass flow controller. The output energy was calculated from the product heating value/energy content. For cost calculations, electricity was assumed to be $0.06/kWh, catalyst cost was $26/L or 800 g of the catalyst (Johnson Matthey Catalysts), hydrogen cost was $2/kg of hydrogen, and weight hourly space velocity for the experiment was 8.75/h.

4.3 Results and discussion

4.3.1 Characterization of the upgraded product compared to bio-oil

The properties of the upgraded product may vary depending on the temperature, pressure, catalyst amount, flow rates of the feed and hydrogen flow during the process. Elemental analysis and properties of bio-oil and the upgraded product (SG gasoline) were compared with conventional gasoline (Tables 4.2 and 4.3). The bio-oil was highly

oxygenated (37%), and this oxygen content was reduced to 8 wt% for the light fraction and 2% after catalytic hydrogenation (Table 4.2). Oxygen content of 2% in the upgraded product (SG gasoline) was comparable to conventional gasoline that consists of 2−5.6% oxygen (Galiasso et al., 2008; SwRI). Similarly, carbon content of bio-oil (50%) increased to 83−85% for the upgraded gasoline, which is comparable to typical gasoline with 84.5% carbon (Galiasso et al., 2008; Scholze and Meier, 2001).

Presence of oxygen results in lower energy density and immiscibility with hydrocarbon fuels (Zhang et al., 2007). Heating value (HV) of the bio-oil from pyrolysis was 36.3 MJ/kg but increased to 46 MJ/kg for the upgraded product and is comparable to typical gasoline of 47 MJ/kg (Galiasso et al., 2008). Moisture content of the bio-oil was 13%, resulting from the original feedstock moisture and the product of dehydration during pyrolysis reactions (Shihadeh and Hochgreb, 2002). However, water was removed during distillation of the bio-oil and during upgrade; water content of the upgraded product was <0.1%. NREL (National Renewable Energy Laboratory) studies showed that additional thermal cracking of bio-oil improved its chemical and vaporization characteristics, resulting in lower water content and lower molecular weight (Zhang et al., 2007; Shihadeh and Hochgreb, 2002). The viscosity of raw bio-oil is 10 cSt, which was reduced to 0.15 cSt for the upgraded product and was comparable to that of gasoline (Table 4.3). Studies of bio-oil viscosity showed that viscosity is lowered by removing water insolubles and by adding alcohol (Sipilae et al., 1998; Boucher et al., 2000).

Table 4.2
Ultimate analysis comparison of bio-oil and upgraded product.

Ultimate analysis	Bio-oil (%)	Bio-oil light fraction (%)	*SG Gasoline 1 (%)	*SG Gasoline 2 (%)	Gasoline (%)
C	50	81	85	83	84.5
H	9.3	10	13	15	13
N	1.5	1.1	–	–	–
S	0.6	–	–	–	<0.0001
O	37	8	2	2	2–6

*SG Gasoline 1 was produced at 110 °C & SG Gasoline 2 was produced at 120 °C (gasoline: Galiasso et al., 2008)

Table 4.3
Physical properties comparison of bio-oil and upgraded product.

Properties	Bio-oil	Bio-oil light fraction	*SG Gasoline 1	*SG Gasoline 2	Gasoline (%)
Heating value (MJ/kg)	36	33	46	46	47.3
Moisture content (%)	13	<0.1	<0.1	<0.1	<0.1
Density (kg/m^3)	920	875	786	787	723
Viscosity (cSt)	10	2.1	0.15	0.15	0.12

*SG Gasoline 1 was produced at 110 °C and SG Gasoline 2 was produced at 120 °C (gasoline: Galiasso et al., 2008)

Bio-oil Light fraction SG Gasoline

Fig. 4.3. Bio-oil upgraded to gasoline.

4.3.2 Distillate analysis and true boiling point curve

Bio-oil distillate below 140 ^{o}C consisted of light fraction hydrocarbons in the C_4–C_{10} range. True boiling point curve (Figure 4.4) shows the distribution of % volume of the bio-oil fractions with temperature. The bio-oil curve is compared to light and heavy crude oil (Benali et al. 2012). The comparison shows that the bio-oil used in this research contains lighter components with lower boiling points. Further, below 140 ^{o}C, 45% fraction was collected and 10% of that was water. Therefore, 35% was upgraded during hydrogenation.

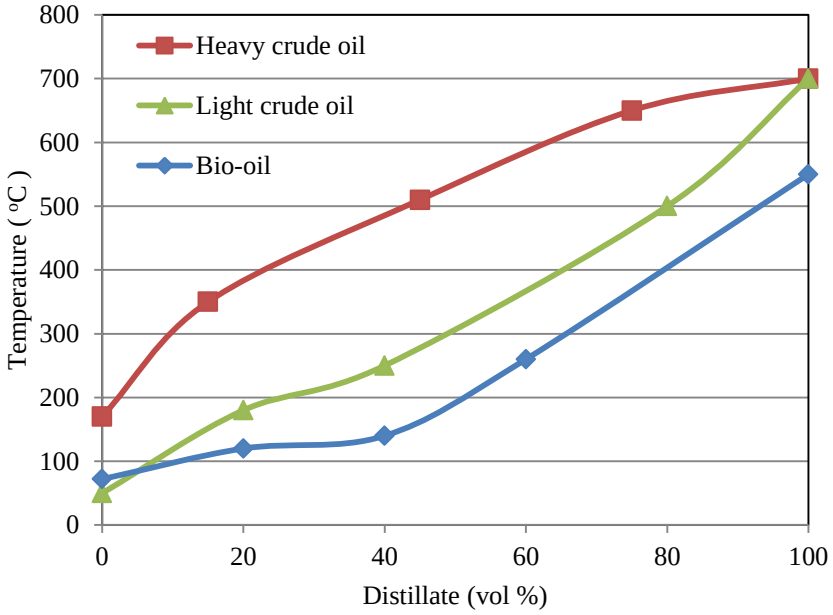


Fig. 4.4. True boiling point curve for bio-oil distillation (light and heavy crude oil by Benali et al., 2012).

Table 4.4
Detailed hydrocarbon analysis of the distillate below 140 ºC.

Composition	Groups	Wt %	Total Wt%
Butane	Paraffins	0.9	
Decane		1.1	2
2-Propanone	Oxygenates	11.7	
2-Pentanone		3.2	
3-Pentanone		0.8	
Butanoic acid, methyl ester		0.8	
3-Penten-2-one		0.8	
2-Pentanone, 3-methyl-		0.9	
Pentanoic acid, methyl ester		0.4	
3-Hexanone		0.6	
2-Hexanone		2.3	
Ethanone, 1-(1H-pyrazol-4-yl)-		1.6	
Cyclopentanone, 2-methyl-		2.1	25.1
1-Pentene, 2-methyl-	Olefin	41.5	
3-Hexene, 2-methyl		0.5	42
Benzene, methyl-	Aromatics	4.3	
Benzene, ethyl-		1.8	
Benzene, 1,3-dimethyl-		5.9	
Benzene, 1-ethyl-2-methyl-		1.7	
Benzene, 1,2,4-trimethyl-		0.9	
Benzene, 1-ethyl-3-methyl-		1.6	
Benzene, 2-propenyl-		0.5	
Benzene, 1-propynyl-		0.4	
Benzene, (2-methyl-1-propenyl)-		0.5	
Benzene, 1-methyl-4-(1-propynyl)-		0.5	
Benzene, (1-methyl-2-cyclopropen-1)-		0.4	18.5
Cyclohexane	Napthene	3.9	
Cyclopropane, octyl		0.5	4.4
Cyclopentene, 3-ethyl-	Nepthene-olefin	0.7	
Cyclohexene, 1,2-dimethyl-		0.5	1.1
Furan, 2,5-dimethyl-	DMF	2.3	
2-S-butyl-furan		1.1	
Benzofuran		1.1	
Benzofuran, 2-methyl-		1.1	
2,3,5-tri-methyl-furan		0.4	5.9
Napthalene		1.0	1.0

Bio-oil from pyrolysis is composed of a complex mixture of alcohols, esters, ketones, lignin-derived phenols, long-chain alkanes, aldehydes, fatty acid methyl esters,

furans, napthalene, amides, and various aromatics described in Chapter 3. However, after distillation, fraction below 140 °C is rich in olefins (42%), oxygenates (25.1%), and aromatics (18%). Other chemicals include paraffins (2%), napthene (4.4%), napthene-olefin (1.1%), both dimethylfurans (DMF) and benzofurans (5.9%), and napthalene (1%). Table 4.4 lists the detailed composition of this light fraction.

4.3.3 Upgraded product at different temperatures and comparison to commercial gasoline

Bio-oil fraction was upgraded at temperatures of 110 and 120 ^{o}C. Both results were similar with minor differences (Tables 4.5 and 4.6). Upgraded product at 110 ^{o}C contained 14.8% paraffins, 21.7% iso-paraffins, and 3% napthene, which increased to 19.4%, 25.8%, and 8.4%, respectively, for the upgraded product at 120 ^{o}C. However, the aromatic decreased from 42.6% to 33.4%, olefin from 4.7% to 3.9%, DMF from 4.7% to 1.3% with the increasing upgrading temperature. Both contained 8% alcohol. At the lower temperature, there were 0.6% oxygenates (ketone) remaining to be hydrogenated whereas, at higher temperature, there were no objectionable oxygenates in the product. Upgraded product consumed 0.005 g H_2/g feed at 120 ^{o}C, and 0.0048 g H_2/g feed at 110 ^{o}C. Based on the reactive present in light fraction (feed), H_2 consumption of 0.0065 g H_2/g feed is required. H_2 consumption was based on percentage reactives that can undergo hydrogenation.

Table 4.5
Hydrocarbon analysis of the upgraded product at 110 °C.

Composition	Groups	Wt %	Total wt %
Pentane	Paraffins	9.4	
Decane		5.4	14.8
Pentane, 2,3-dimethyl	Isoparaffins	21.7	21.7
Benzene, methyl-	Aromatics	11.2	
Benzene, ethyl		6.3	
Benzene, 1,3-methyl		20.8	
Benzene, 1-ethyl-3-methyl		4.3	42.3
2-Pentene	Olefin	4.7	4.7
2-Pentanol	Alcohol	7.9	7.9
Furan, 2,5-dimethyl	DMF	4.7	4.7
Cyclohexane	Napthene	3	3
2-Pentanone	Oxygenate (Ketone)	3.6	0.9

Table 4.6
Hydrocarbon analysis of the upgraded product at 120 °C.

Composition	Groups	Wt%	Total wt%
Pentane	Paraffin	16.5	
Decane		2.9	19.4
Pentane, 3-methyl	Iso-paraffin	25.8	25.8
Di-methyl-1 pentene	Olefin	1.8	
Pentene, 4-dimethyl		2.1	3.9
Benzene	Aromatics	3.8	
Benzene, methyl-		4.2	
Oxetane, 2-ethyl-3-methyl		2.6	
Benzene, ethyl-		17.8	
Benzene, 1,4-dimethyl		3.6	
Benzene, 1-ethyl-2-methyl		1.4	33.4
2 Butanol, 3 methyl	Alcohol	2.9	
2 butanol		4.9	7.8
Furan, 2,5-dimethyl-	DMF	1.3	1.3
Cyclohexane, methyl	Napthene	2.2	
Cyclohexane, ethyl		6.2	8.4

Bio-oil, its distilled light fraction, and the upgraded products of two temperatures are compared (Figure 4.5). Most importantly, after catalytic hydrogenation, the oxygenates decreased from 37 wt% in bio-oil to 25 wt% in the bio-oil light fraction and to 2 wt% in the final product. Aromatics increased from 12 wt% in bio-oil, to 18.5 wt% in the light fraction, and 42.6 wt% in the upgraded product at 110 ^{o}C, and 33.4 wt% in the upgraded product at 120 ^{o}C. Some olefins in the bio-oil light fraction were hydrogenated to paraffins, resulting in increase in paraffins from 2 wt% to 14.8 wt% and 19.4 wt% in the respective upgraded products. Similarly, some paraffins went through isomerization to form isoparaffins during hydrogenation (Bernard et al. 2007), resulting in 21.7 wt% and 25.8 wt% isoparaffins in the upgraded products

Gasoline produced from bio-oil in this research was compared with commercial gasoline from Shell and Kroger (Figure 4.6). Commercial gasoline contains 35−70 wt% saturates including both paraffins and isoparaffins, olefins (1−15 wt%), aromatics (14−56 wt%), napthene (1−11 wt%), naptheneolefin (<1 wt%), and alcohols (up to 6 wt%) (SwRI; Vasquez, 2009). SG Gasolines 1 and 2 are within the ranges of commercial gasoline standards. With increasing temperatures of 110 to 120 ^{o}C, SG gasoline also contained DMF of 4.7 wt% and 1.3 wt%. A study at the University of Birmingham, UK, showed similar combustion performance and regulated emissions of DMF in direct injection engine study as gasoline (Zhong et al., 2010). High aromatic in gasoline is good for high octane number (resistance to knock and burns smoothly), where mono-aromatics are better than poly-aromatics (SwRI). High poly-aromatics are predicted to have high emissions of volatile organic compounds (VOC), No*x* and other toxics and are

penalized by the Environmental Protection Agency (EPA). Gasoline produced in this research contained all mono-aromatics (Tables 4.5 and 4.6). Further, SG gasoline contained 8% alcohol that was either butanol or pentanol instead of ethanol. This is beneficial to the biofuel, because long-chain alcohols possess major advantages over the currently used ethanol as bio-components for gasoline, including higher energy content, better engine compatibility, and less water solubility (Yang et al., 2010).

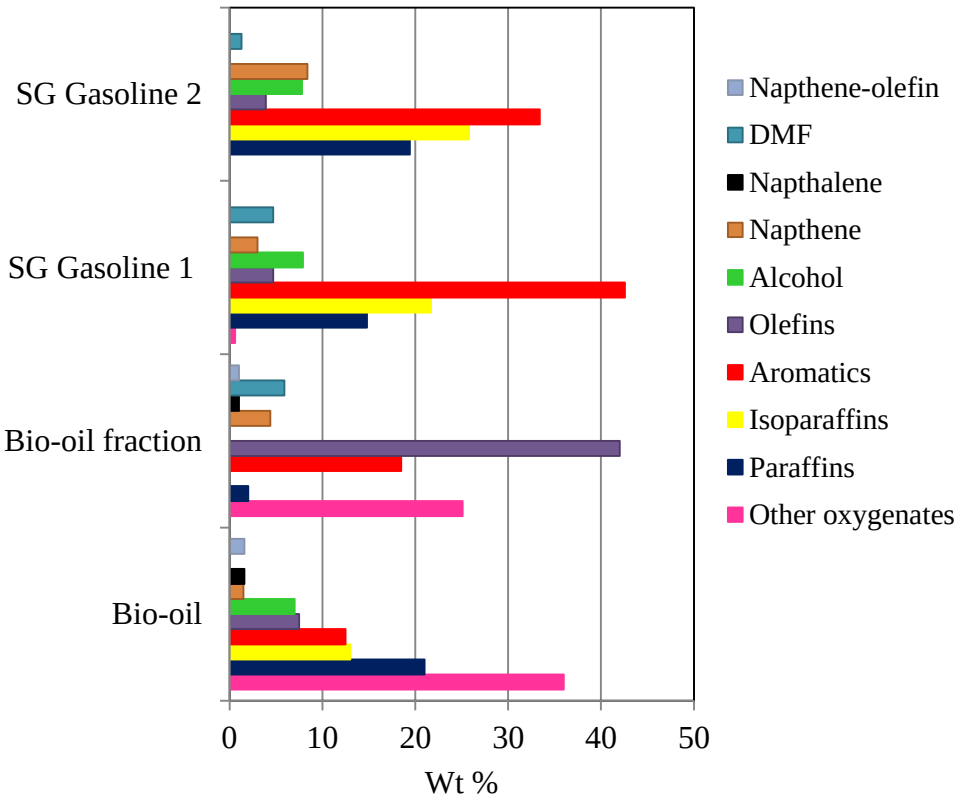


Fig. 4.5. Bio-oil comparison to upgraded product **(**SG Gasoline 1 was produced at 110 °C and SG Gasoline 2 was produced at 120 °C).

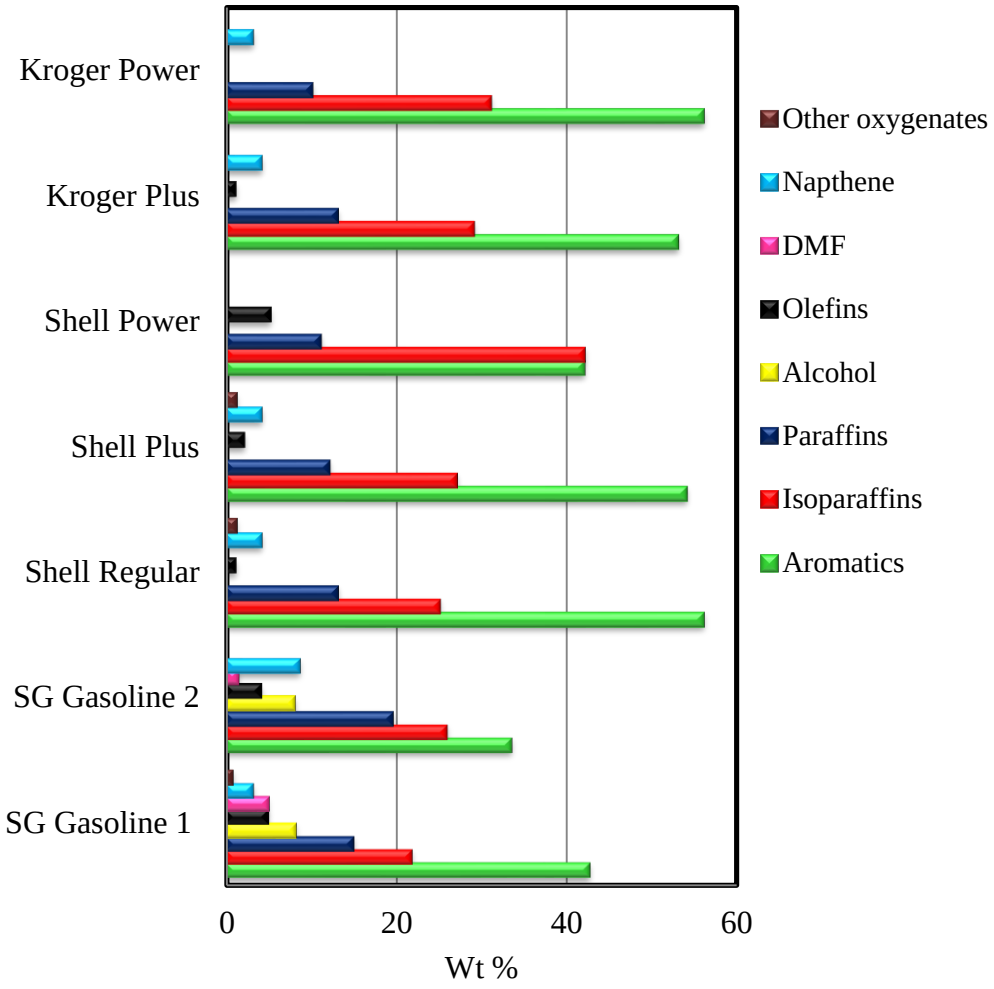


Fig. 4.6. Upgraded product comparison to commercial gasoline (Kroger and Shell gasoline data by Vasquez, 2009).

Overall, this novel upgrade technology has various benefits compared to past technologies; there is very little water formation, no CO or CO_2 in the product, and no mass loss from carbon; therefore, hydrocarbon yield is high. The process is energy efficient (110–120 °C, reaction temperature) in comparison to previous hydrogenation

products using nickel or cobalt molybdenum or zeolite catalytic cracking (300−600 °C, reaction temperature). Finally, the product is stable for storage, unlike bio-oil.

4.3.4 Thermal/oxidation stability of the gasoline from bio-oil

A thermal stability test measures oxidation stability of gasoline by determining potential gum in the fuel. Typical gasoline may have an induction period of 600 min or higher, depending on its stability. This means the gasoline would have the tendency to form gum as it is oxidized by consuming oxygen from an oxygen-rich-environment under 100 °C, beyond the induction period of 600 min (ASTM D525). To be considered stable for use in engines, gasoline must pass this standard. Gasoline produced in this research passed the 600-min induction period when kept under oxygen-rich environment for 24 h (Figure 4.7). Therefore, SG gasoline was considered to have an induction period of 1,440 min or greater under an oxygen-rich environment at 100 °C.

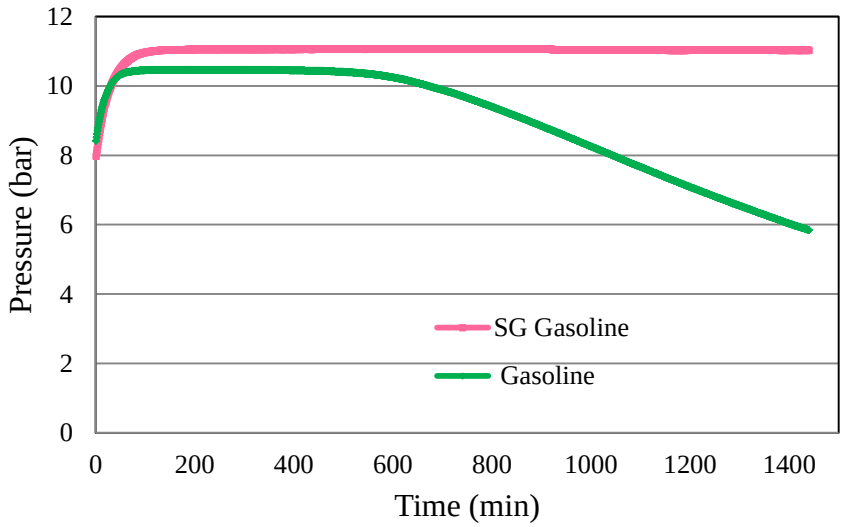


Fig. 4.7 Thermal stability of SG gasoline from bio-oil (source for gasoline: SwRI).

As discussed in Chapter 3, bio-oils have severe problems with stability. Even after distillation, the light fraction of bio-oil oxidizes when stored under regular atmospheric condition. As the bio-oil fraction oxidizes, the color changes from light yellow to black, and forms gum. However, during the oxidization stability test, the upgraded product passed the stability test and did not oxidize or form gum in an oxygen-rich environment.

4.3.5 Energy balance and cost analysis for bio-oil upgrade

Figure 4.8 presents energy and cost distribution of bio-oil upgrade through catalytic hydrogenation. The energy and cost distribution were calculated based on the experimental conditions of this work, and calculation specifications are presented in Section 4.2.6. If the conditions are changed, these distributions may vary. The main factors that affect the energy and cost distributions of the upgrade process follow: bio-oil feed flow rate, hydrogen flow rate/hydrogen usage, process temperature, stirring speed during the process, catalyst amount, catalyst life, and large-scale production. From the current experimental conditions, feed obtained from bio-oil distillation accounted for the highest energy content (35%) and cost (36%), followed by the greatest energy consumption from the heater (22%) of the process. Continuous stirring accounted for 12% of the energy consumed and cost. With the current conditions, there was an energy loss of 26% in the system based on (product energy/feed energy + equipment energy).

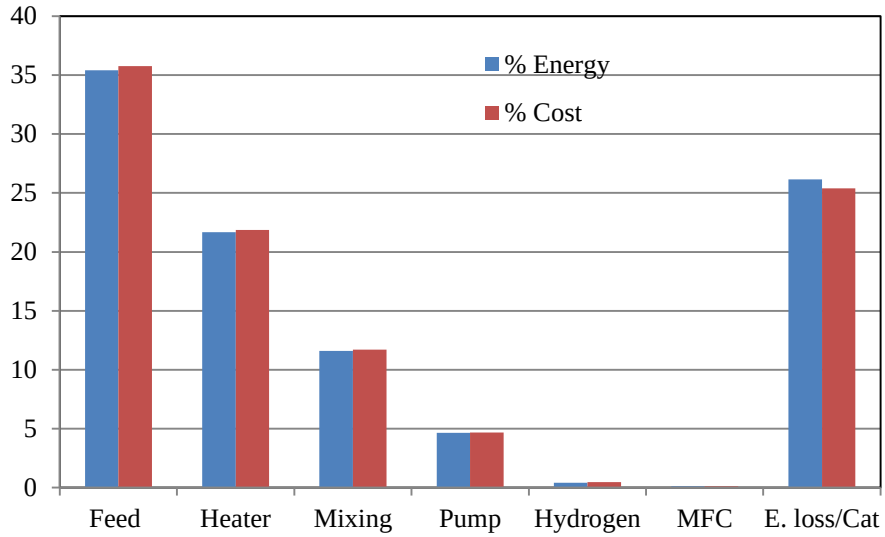


Fig. 4.8. Bio-oil upgrade energy and cost distribution.
(MFC−mass flow controller, E−energy, Cat−catalyst)

Catalyst accounted for 25% of the cost, with catalyst price being $26/L (800 g). According to JMC these catalyst may be used for weeks in a continuous experiment. Regeneration costs $42/L of catalyst, which reduces cost in the long run. Energy and cost of pump usage were less than 5% of the total. Further, hydrogen usage (0.5% energy and 1% cost), and the mass flow controller (MFC) energy were comparatively low. That was mainly because this process used a low flow rate (15 mL/min) of hydrogen and a low pressure (33.5 bar) compared to past studies that used 69 to 345 bar (1000−5000 psig). The complete system from biomass to gasoline is analyzed and the distribution of energy and cost of each step of the process are given in Section 5.

4.4 Conclusions

Bio-oil oxygen content decreased from 37 wt% to 2 wt%, carbon content increased from 50 wt% to 84 wt%, and hydrogen content increased from 9% to 14 wt% after catalytic hydrogenation; SG gasoline is comparable to commercial gasoline having 84.5% carbon, 13% hydrogen, and 2−6% oxygen. Heating value of the bio-oil from pyrolysis increased from 36.3 MJ/kg to 46 MJ/kg for the upgraded products, which is comparable to the HV of commercial gasoline (47 MJ/kg).

Aromatics comprised 12 wt% in bio-oil; 18.5 wt% in the light fraction, and 42.6 wt% in the upgraded product at 110 ^{o}C and 33.4 wt% in the upgraded product at 120 ^{o}C. Some olefins in the bio-oil light fraction were hydrogenated to paraffins, resulting in increase in paraffins from 2 wt% in the light fraction to 14.8 wt%, and 19.4 wt% in the upgraded products. Similarly, some paraffins went through isomerization to form isoparaffins during hydrogenation reaction, resulting in 21.7 wt% and 25.8 wt% isoparaffins in the upgraded products.

Upgraded product at 110 ^{o}C consisted 14.8 wt% paraffins, 21.7 wt% iso-paraffins, and 3 wt% napthene; these values increased to 19.4 wt% 25.8 wt% and 8.4 wt%, respectively, for the product upgraded at 120 ^{o}C. However, the aromatics decreased from 42.6 wt% to 33.4 wt%, olefin decreased from 4.7 wt% to 3.9 wt%, and DMF decreased from 4.7 wt% to 1.3 wt% with the increasing upgrading temperature. Both upgraded gasolines from different temperature contained 8% alcohol. At the lower temperature, there were 0.6% oxygenates (ketone) remaining to be hydrogenated fuel whereas, at higher temperature, there were no objectionable oxygenates (ketones, esters,

acids) or di-olefins in the product. Gasoline produced at both process temperatures in this research are within the hydrocarbon ranges of commercial gasoline standards.

Gasoline produced in this research (110 ^{o}C) passed the 600-min induction period when kept under oxygen rich environment for 24 h. This gasoline was considered to have an induction period of 1,440 min or greater under oxygen-rich environment at 100 ^{o}C. Therefore, the upgraded product was considered a stable product similarly to standard gasoline. Because bio-oil has been known for its unstable character and tendency to oxidize under regular atmospheric conditions, this solves a major problem,

Feed obtained from bio-oil distillation accounted for the highest energy content (35%) and cost (36%), followed by the greatest-energy-consumption from the heater (33%). Catalyst accounted for 25% of the cost, with catalyst price being $26/L (800 g). Continuous stirring accounted for 12% of the energy consumed and cost. With the current conditions, there was an energy loss of 26% in the system. Energy and cost of pump usage were less than 5%. Hydrogen and mass flow controller contributed to less than 1% energy and cost.

5. COMPARISON OF BIOLOGICAL AND THERMAL CONVERSION PATHWAYS

5.1 Introduction

In the previous chapters, the concepts and experimental work on both biological and thermal conversions of lignocellulosic biomass to biofuel were discussed. Biological conversion requires removal of lignin, making cellulose and hemicellulose available for saccharification and fermentation to sugars and ethanol, respectively. Lignin is not biologically converted to ethanol. In contrast, thermal conversion involves depolymerization and fragmentation of the entire biomass; all cellulose, hemicellulose, and lignin are converted to bio-oil, syngas, and bio-char. Table 5.1 presents the sequence of activities for both pathways.

Table 5.1
Biological and thermal conversion pathways for biofuel production from biomass.

Biological/biochemical conversion pathway	Pyrolysis – depolymerization & fragmentation pathway
1. Remove lignin and disrupt structure	1. Moisture evolution (<220 ^{0}C)
2. Hydrolyze cellulose and hemicellulose to glucose, xylose, arabinose, mannose	2. Hemicellulose decomposition (220−315^{0}C)
3. Ferment sugars to bio-ethanol	3. Cellulose decomposition (315−400 ^{0}C)
	4. Lignin degradation (>400 ^{0}C)

This chapter compares biological and thermal conversion pathways used in this research in terms of process efficiency, brief cost distribution, and feedstock characterization. Overall process yields, mass and energy losses, product values, and feedstock usages are all discussed.

5.2 Methods of calculations and data presentation

5.2.1 Energy and cost calculation specifications for biological conversions

Input energy was calculated from pretreatment, saccharification, fermentation, distillation and biomass. Output energy was based on the ethanol energy content of 29.7 MJ/kg. Table 5.2 presents the power ratings of all equipment used for biological conversion calculations.

Table 5.2
Energy consumption of equipment used for biological conversion.

Process	Equipment	Power rating (W)
Pretreatment	Ultrasonic (25 min)	400
Pretreatment	Pressure reactor (1 h)	770
All processes	Centrifuge (30 min)	360
Saccharification/fermentation	Incubator shaker (5 days)	360
Distillation	Distillation heater (1 h)	770

For process cost specifications, the following were used: (1) mixture of cellulase and hemicellulase enzyme solution was $10−20/kg (Genencor Inc.); (2) yeast strain was $760/tonne (Cangzhou Huayou Import & Export Trade Co., Ltd.); (3) electricity was $0.06/kWh; (4) biomass was $40/dry tonne; (5) both biological and thermal conversions had a starting biomass of 1,538 g (based on 200 g SG gasoline production); (6) final yield was calculated based on 20−30 dry ton/(acre·yr) of sweet sorghum (University of

Florida, Florida); (7) cost of the product was calculated with a 15% profit before tax; and (8) cost calculation was based on operating cost.

5.2.2 Energy and cost calculation specifications for thermal conversions

Input energy was calculated from pyrolysis, distillation, catalytic hydrogenation, and biomass. Output energy was from the upgraded product energy content of 47 MJ/kg. Table 5.3 presents the wattage/power rating of all equipment used for thermal conversion calculations.

Table 5.3
Energy consumption of equipment used in thermal conversion.

Process	Equipment	Power rating (W)
Pyrolysis	Pressure reactor (75 min)	3,600
Distillation	Distillation heater (1 h)	770
Upgrade	Reactor heater (6.6 h)	210
Upgrade	Reactor stirrer (6.6 h)	135
Upgrade	Feed pump (6.6 h)	30
Upgrade	Mass flow controller (6.6 h)	0.78

For process cost specifications, the following were used: (1) electricity was assumed to be $0.06/kWh; (2) catalyst cost was $26/L or 800 g of the catalyst, and catalyst cost including regeneration factor was $40/L (Johnson Matthew Catalyst); (3) biomass was $40/dry ton; (4) final yield was calculated based on 7−8 dry ton/(acre·yr) of switchgrass (Auburn University, Alabama), and (5) cost of the product was calculated with a 15% profit before tax. Other specifications of the upgrade process were discussed in Section 4.2.6.

5.3 Results and discussions

5.3.1 Comparisons of energy and cost distributions for biological and thermal conversions

Calculations for both biological and thermal conversion processes were based on the same amount of initial biomass (1,538 g). However, as described in Chapters 2 and 3, for the biological conversion process, the biomass used was sorghum (14.9 MJ/kg), whereas for the thermal conversion process, the biomass was switchgrass (19.8 MJ/kg). For biological conversion: distribution of mass from biomass resulted in: ethanol (11%), sugar (12%), residue after experiment (57%), and mass loss (20%). For biological conversion: distribution of energy resulted in ethanol (22%), sugar (14%), residue after experiment (54%), and energy loss (10%) (Figure 5.1). Mass and energy distribution of products from biomass for thermal conversion was described in Chapter 3. The energy and cost distributions from the biological and thermal conversion processes are presented in Figures 5.2 and 5.3. For biological conversions, lengthy saccharification and fermentation time of 5 days consumed most energy, including that used for shaking and heating at 50 ^{o}C and stirring at 125 rpm for saccharification, as well as heating at 32 ^{o}C and stirring at 150 rpm for fermentation. Saccharification and fermentation in combination with distillation consumed 22.5% and 17%, respectively of the total energy. Pretreatment consumed the least energy (5%), because it was a short pretreatment of 1.25 h. Energy loss was high (45%) because of the low yield (11%) ethanol, and 57% of biomass that was not used during ethanol production.

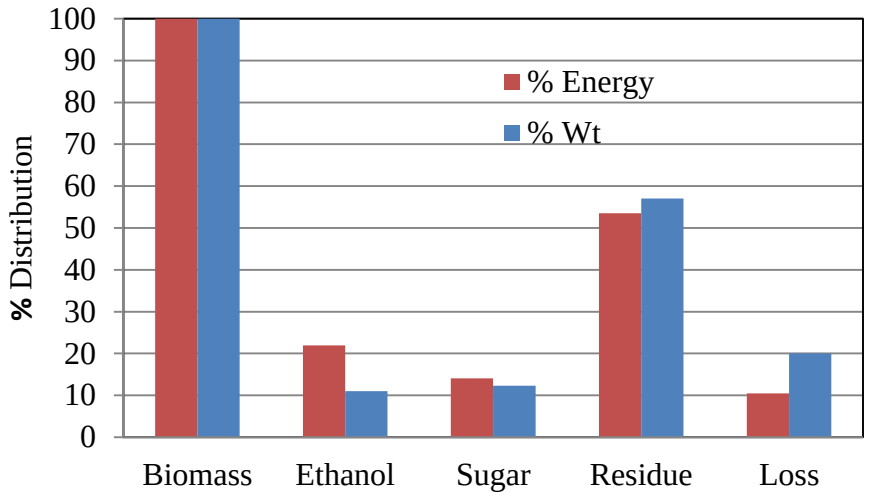


Fig. 5.1. Wt % and energy distribution for biological conversion process.

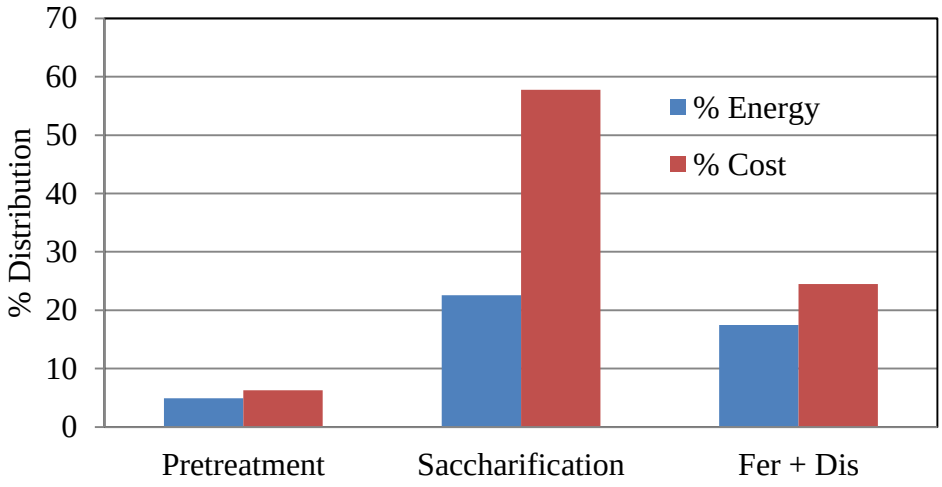


Fig. 5.2. Energy and cost distribution for biological conversion.
(Fer = fermentation and Dis = distillation)

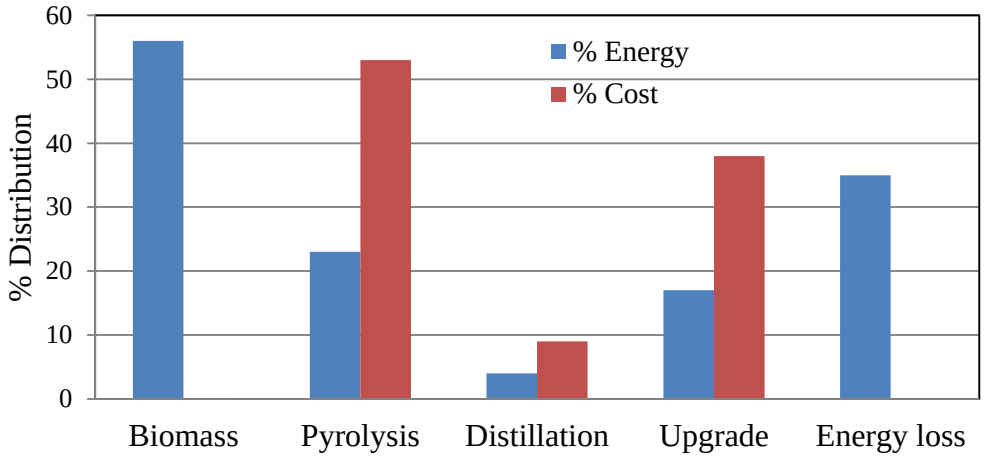


Fig. 5.3. Energy and cost distribution for thermal conversion.

In comparison to the biological conversion of biomass to ethanol, thermal conversion of biomass to gasoline had 35% energy loss (Figure 5.3). Energy loss was less for thermal (35%) than for biological (45%), because the biomass (switchgrass) used for thermal conversion had higher energy content (19.8 MJ/kg) and operating conditions were efficiently optimized. However, biomass contributed similar % energy to the individual processes; thermal conversion process with 56% (Figure 5.3), and biological conversion with 55% biomass energy (derived from Figures 5.1 and 5.2). Further, the by-products produced during thermal conversions (syngas and bio-char) are also high in energy (discussed in Chapter 3). So, the total output energy for the thermal process was 33% higher, and as a result, there was lower energy loss. From the three-step process for converting biomass to switchgrass gasoline, pyrolysis consumed the highest energy (23%), followed by upgrade of bio-oil to gasoline (17%), and lastly, distillation (4%) (Figure 5.3). The energy consumed for both upgrading and distillation was comparatively lower because of the lower temperature for both processes (110 ^{o}C and

140 ^{o}C, respectively) in comparison to pyrolysis at 400 to 600 ^{o}C. Further, production of a higher energy content product, gasoline (47 MJ/kg) reduced the energy loss for thermal conversion versus bio-ethanol (29.7 MJ/kg) for the biological conversion process. The product yield was 2% higher for thermal conversion (13 wt% SG gasoline) than for biologic conversion (11 wt% ethanol), which added to the energy value of the product (Table 5.4 and Figure 5.4).

For biological conversions, saccharification was the greatest cost (58%). This cost was mainly due to high prices of $10−20/kg of cellulase and hemicellulase enzymes that contributed enzyme cost of 29−45% respectively; saccharification operation accounted for 22% of the cost. Fermentation and distillation contributed to 25% of the cost, which included costs of fermentation 19%, distillation 2.5%, and yeast 2% ($760/tonne of yeast). Pretreatment had the lowest contribution to cost (6.3%), because it did not involve expensive enzymes or chemicals. For the biological conversion to make a 15% profit, bio-ethanol would have to be sold at $2.5/gallon before tax which is equivalent to $4/gallon gasoline.

On the other hand, for thermal conversion, pyrolysis accounted for the highest fraction of the cost (53%). This cost was due to high temperature (400 to 600 ^{o}C) required for biomass conversion to bio-oil. Cost distribution for upgrade and distillation were 38% and 9%, respectively. The upgrade cost (38%) can be improved by varying some of the conditions, as discussed in Chapter 4. Energy loss for thermal conversion was 35%. However, for the thermal process to make a 15% profit, upgraded product (switchgrass gasoline) would have to be sold at $3.7/gallon before tax. The major cost-

related issues for biological and thermal conversion were enzyme and high pyrolysis temperature, respectively. Since, 29–45% of the biological conversion cost could come from enzymes, the biological process is in need of less expensive microbes to reduce this cost. For thermal conversion, lower pyrolysis temperature (400 and 500 °C) oil and optimizing the upgrade variables could reduce cost.

5.3.2 Conversion and yield comparison for biological and thermal pathways

Most of the conversion data for lignocellulose to bio-ethanol were discussed in Chapter 2; however, they are summarized in Table 5.4. For the biological conversion process, ethanol yield was 11% from the whole lignocellulosic biomass, sweet sorghum (Table 5.4). This is slightly lower than the overall process yield of 13% for thermal conversion process (Figure 5.4).

Table 5.4
Conversion efficiency for the biological process.

Conversion and yield	Wt %
Lignocellulosic conversion to glucose efficiency	80–89
Lignocellulosic conversion to xylose efficiency	40–48
Fermentation conversion to ethanol (ethanol/sugar)	45
Total process yield (ethanol/biomass)	11

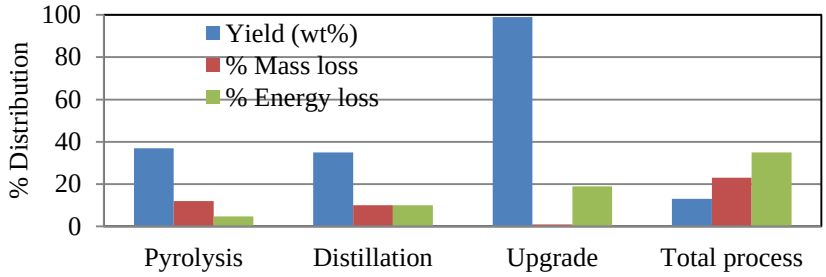


Fig. 5.4. Thermal conversion process yield, mass loss and energy loss at each step.

For thermal conversion process, biomass to bio-oil yield was 37% from pyrolysis. A light fraction was collected with a yield of 35% during distillation. And finally, this fraction was upgraded to gasoline with almost no mass loss. Therefore, the total process had 13 wt% yield of switchgrass gasoline from biomass. The energy loss was 5%, 10%, and 11% for pyrolysis, distillation and upgrade, respectively. The total process had 35% energy loss. Mass loss for the complete process was 23%. Pyrolysis had the greatest mass loss of 12%, followed by 10% for distillation and 1% for upgrade.

5.3.3 Comparison of feedstock characteristics for processes

Both switchgrass and sorghum are high-energy perennial crops and are easy to grow, with switchgrass production of 7−8 tonne/(acre·yr) and sweet sorghum production of 20−30 tonne/(acre·yr) (Missaoui et al., 2005; Wu et al., 2010). However, switchgrass adds higher energy value to processes, due to its higher energy content of 19.8 MJ/kg, versus 14.9 MJ/kg for sweet sorghum (Table 5.5). The high energy content of switchgrass is apparent from the ultimate analysis of the biomass. High energy content mostly comes from the carbon and hydrogen content of the biomass. Ultimate analysis shows that the carbon (42 wt%) and hydrogen (6.1 wt%) content of switchgrass were higher than carbon (38 wt%) and hydrogen (5.6 wt%) of sweet sorghum (Table 5.5). Oxygen content was higher for sweet sorghum (55.3%) versus switchgrass (47.4 wt%). This suggests that switchgrass may be a suitable biomass for thermal process, to obtain a product with lower oxygen after pyrolysis, because the original biomass had lower oxygen content. As a result, upgrade may be easier. Similarly, structural analysis shows lower lignin content in sweet sorghum (11%) than in switchgrass (18.8%). This indicates

that sweet sorghum may be a suitable feedstock for biological conversion process, because lignin is not biologically converted to sugars and cannot be used for ethanol production. However, lignin can be thermally depolymerized and fragmented during thermal conversion process (Chiaramonti et al., 2003). Also, compared to switchgrass (32% glucan), sweet sorghum contains higher glucan (48%), which may be suitable for ethanol production.

Table 5.5
Comparison of feedstock characteristics of switchgrass and sweet sorghum.

Proximate analysis	Moisture (%)	Volatile combustible matter (%)	Ash (%)	Fixed carbon (%)
Switchgrass	8.4	84.2	3.9	11.9
Sweet sorghum	6.7	69.3	9.1	14.9

Ultimate analysis	N%	C%	H%	S%	O%
Switchgrass	0.4	42	6.1	0.1	47.4
Sweet sorghum	0.9	38	5.6	0.2	55.3

Structural analysis	Glucan (%)	Xylan (%)	Lignin (%)	Extractives (%)
Switchgrass	32	19.2	18.8	18.5
Sweet sorghum	48	19.7	11	7

Heating value	MJ/kg
Switchgrass	19.8
Sweet sorghum	14.9

Proximate analyses show higher percentages of volatile combustible matter (VCM) in switchgrass (84.2%) versus sweet sorghum (69.3%). Also, the ash content is

lower in switchgrass (3.9%) compared to sweet sorghum (9.1%). Studies showed high VCM and low ash content favor higher bio-oil yield (Mullen and Boateng, 2008). Therefore, switchgrass may be a favorable biomass for thermal conversions, and sweet sorghum may be favorable for biological conversions.

Both biological and thermal conversion processes were used in this research. Table 5.6 compares the biological and thermal conversion pathways in relation to processes and feedstocks used this research.

Table 5.6
Comparison of biological and thermal (pyrolysis) pathways for conversion of lignocellulose to biofuels in this research.

Comparison items	Biological process: biomass to bio-ethanol	Thermal process: biomass to gasoline
Process product yield	11 wt%	13 wt%
Energy loss for complete process	45%	35%
Mass loss during process	12%	23%
Cost with 15% profit	$2.5/gallon (gasoline equivalent; $4/gallon)	$3.7/gallon
Biomass contributed to energy input	55%	56%
Highest cost of process	from enzyme	from pyrolysis
Length of process	5 days, 4 hrs	8.75 hrs
Production (L/ha·yr)	4,335−4,558	2,186−2,499

5.3.4 Sensitivity analysis

Sensitivity to the product selling price was mainly due to enzyme price of $10−$20/kg for biological conversion process. When enzymes were $10/kg, enzyme cost was 29% of the total biological process with ethanol selling price of $2.5/gallon, for a 15% profit before tax. However, when enzymes were $20/kg, enzyme cost was 45% of

the total process with ethanol selling price of $3.2/gallon. On the other hand, for thermal process, when upgrading catalyst was $26/L, catalyst cost was 25% of the upgrading cost with switchgrass gasoline selling price of $3.7/gallon. However, when regeneration cost was included for catalyst ($42/L), catalyst cost was 36% of the upgrading cost with gasoline selling price of $4/gallon. Advantage of catalyst over enzyme is that catalyst can retain its performance ability for weeks, and after regeneration, one may not have to buy new catalyst. However, with enzymes there is no regeneration option.

5.4 Conclusions

Based on the biological and thermal pathways used in this research, thermal conversion was comparatively effective in terms of process efficiency and cost. This conclusion is supported by the relatively lower energy loss of 35% for thermal conversion processes versus 45% energy loss for biological conversion processes. The biological process was lengthy, and it used expensive enzymes that resulted in negative energy and high cost, respectively. However, energy efficiencies for the biological conversion can be increased with process condition optimization (condition and dosage for enzyme performance, combining saccharification and fermentation to reduce experiment duration, using different microbes to increase product yield, and using the residue after biological conversion for energy production). For the lab scale ethanol production, for 15% profit, cost of ethanol was $2.5/gallon with a gasoline equivalent cost of $4/gallon. This high cost can be lowered, if naturally occurring microbes can be used or microbe cost (29−45% of process cost) can be lowered. Process energy for thermal conversion was (44%) and biological (45%) for lab scale production of

switchgrass gasoline versus bioethanol, respectively. In addition to the high value product gasoline, syngas and bio-char are also high-energy by-products produced during the thermal conversion processes, and they added to the final energy from the complete thermal process. Therefore, for a 15% profit, switchgrass gasoline cost was $3.6/gallon for the thermal conversion process.

Based on the process pathways followed in this research, biological conversion had yields of 11% ethanol from sweet sorghum, whereas thermal conversion had yields of 13% gasoline from switchgrass. Comparisons of feedstock characteristics showed switchgrass and sweet sorghum to be suitable biomass for thermal and biological conversions processes, respectively. With these yield data, biological conversion process can produce 4,335−4,558 L bioethanol/(ha·yr). Thermal conversion can produce 2,186−2,499 L SG gasoline/(ha·yr).

6. OVERALL CONCLUSIONS AND RECOMMENDATIONS

Biological conversion of first-generation biomass (sweet sorghum juice) resulted in the following conclusions.

- Ethanol yield was 0.065 g/g of juice, and ethanol production rate was 1.8 g/(L·h) for Variety 1 (Umbrella). For Variety 2 (M-81E), ethanol yield was 0.072 g/g of juice, and ethanol production rate was 1.6 g/(L.h). In terms of energy efficiency, V-1 may be a better crop overall, because of its higher rate of ethanol production and shorter maturation period. In terms of ethanol yield, V-2 may be a better choice.
- Ethanol fermentation efficiency varied among the four pre-fermentation preparations. Fermentation efficiencies for frozen, autoclaved, and juice containing 25% sugar were greater than 90%. Juice containing 30% sugar had lower efficiency (79%) because fermentation did not go to completion.

Biological conversion of second-generation biomass (lignocellulosic sweet sorghum) resulted in the following:

- Cellulose and hemicellulose concentrations were increased by 35% and 15% with the hot-water treatment and 49% and 25% with ultrasonication + hot water treatment, respectively, increasing exposure of cellulose and hemicellulose to enzymatic hydrolysis. There was an increase of 15% and 7% for cellulose to glucose and hemicellulose to pentose and hexose, respectively, with ultrasonication + hot water pretreatment versus only hot water treatment.
- The efficiency of cellulose conversion to glucose was greatest when Accellerase 1500 was combined with Accellerase XC enzyme (89%), followed by Accellerase

1500+BG (84%), Accellerase 1500+XY (83%), and Accellerase 1500 (82%). The hemicellulose conversion to xylose and arabinose was greatest when Accellerase 1500 was used in combination with Accellerase XC enzyme (48%), followed by Accellerase 1500+XY (40%).

- Based on cellulosic conversion, ethanol yield in this study varied from 3.2 g to 4.2 g ethanol per 100 g of sweet sorghum biomass.

Comparison of conversion of first- and second-generation biomass to bioethanol resulted in the following.

- This study yielded 1,537−2,273 L ethanol/(ha·yr) for first-generation biomass (sweet sorghum juice), and 4,335−4,558 L ethanol/(ha·yr) from whole lignocellulosic sweet sorghum biomass, without the xylose sugars conversion to ethanol.

Thermal (pyrolysis) conversion of lignocellulosic switchgrass at different temperatures resulted in the following.

- Bio-oil and syngas yields increase, whereas bio-char yield decreases with increasing temperature of pyrolysis. From pyrolysis at 600 ^{0}C, product yield was 37% bio-oil, 26% syngas, and 25% bio-char. However, at 400 ^{0}C pyrolysis, product yield was 22% bio-oil, 8% syngas, and 56% bio-char.
- Efficiency of pyrolysis improved with the pyrolysis temperature; product yield increased from 78% at 400 ^{0}C to 88% at 600 ^{0}C. From pyrolysis at 400 ^{0}C, energy distribution was 33% from bio-oil, 11% from syngas, and 56% from bio-char; energy distribution from pyrolysis at 600 ^{0}C was 47% from bio-oil, 28% from syngas, and 25% from bio-char.

Characterization of pyrolysis products; bio-oil, syngas and bio-char resulted in the following.

- Bio-oil was highly oxygenated (37 wt%). It had a heating value of 36.3 MJ/kg and viscosity of 10 cSt. The oil phase is a complex mixture of hydrocarbons; alkanes (36%), phenols (20.5%), aromatics (12.4%), alcohols (7.4%), ketones (5.1%), and esters and acids (11%).
- For syngas, heating values of CO, C_2H_4, C_2H_6, and C to CO_2 conversion increase, whereas heating values of H_2 and CH_4 decrease at higher temperature, owing to decrease in the volumes of the latter products produced at higher temperatures. This results from the compositional variations of the syngas components; CH_4, and H_2 production decrease whereas CO, CO_2, C_2H_4 and C_2H_6 production increase with pyrolysis temperature.
- The fixed carbon increased and volatile matter content of bio-char decreased with increasing temperature of pyrolysis. Bio-char surface area increased from 0.1 m^2/g at 400 ^oC to 1.0 m^2/g at 600 ^oC pyrolysis.

Bio-oil upgrade to gasoline resulted in the following.

- Bio-oil oxygen content decreased from 37 wt% to 2 wt%, carbon content increased from 50 wt% to 84 wt%, and hydrogen content increased from 9 wt% to 14 wt% after catalytic hydrogenation that resulted in a fuel that was comparable to gasoline having 84.5% carbon, 13% hydrogen, and 2−6% oxygen. Heating value of the bio-oil from pyrolysis increased from 36.3 MJ/kg to 46 MJ/kg for the upgraded product and is comparable to HV of gasoline (47 MJ/kg).

- Upgraded product at 110 ^{o}C consisted 14.8% paraffins, 21.7% iso-paraffins, and 3% napthene, which increased to 19.4%, 25.8%, and 8.4%, respectively, for the upgraded product at 120 ^{o}C. However, the aromatic decreased from 42.6% to 33.4%, olefin from 4.7% to 3.9%, DMF from 4.7% to 1.3% with the increasing upgrading temperature. Both contained 8% alcohol. At the lower temperature, there were 0.6% oxygenates (ketone) remaining to be hydrogenated whereas, at higher temperature, there were no objectionable oxygenates in the product. Gasoline produced in this research is within the hydrocarbon ranges of commercial gasoline standards for both process temperatures.
- Gasoline produced in this research passed the 600-min induction period when kept under an oxygen-rich environment for 24 h. Therefore, the upgraded product was considered a stable product and did not undergo oxidation; it performed similarly to standard gasoline over time.
- For energy and cost for the bio-oil upgrade operations, heating required the highest-energy-consumption (26%) with cost (22%), followed by catalyst cost of 25%. Continuous stirring accounted for 14% of the energy and 12% of the cost; energy from pump, hydrogen usage and mass flow controller were the low. There was an energy gain of 11% for the complete upgrading process.

Biological and thermal conversion processes comparison resulted in the following.

- In terms of process efficiency, thermal conversion had lower energy loss of 35%, versus 45% energy loss for biological conversion processes.

- Highest cost came from enzymes for biological conversion and from pyrolysis for thermal conversion process.
- For biological conversion pathway, cost of ethanol was $2.5/gallon ($4/gallon for gasoline equivalent), and for thermal conversion pathway, cost of switchgrass gasoline was $3.7/gallon, both with a 15% profit before tax.
- Based on this research process, biological conversion process had yields of 11 wt% ethanol from sweet sorghum, and the thermal conversion process had yields of 13 wt% gasoline from switchgrass. With these yield data, the biological conversion process can produce 4,335−4,558 L bioethanol/(ha·yr) land. The thermal conversion process can produce 2,186−2,499 L gasoline/(ha·yr) land.

Recommendations from this research are as follows.

- Study pentose-specific microbes (e.g. *Zymomonus Mobilis*) that can be used to convert pentose sugars (xylose) to ethanol; evaluation of pentose conversion to ethanol was not part of this research.
- Assess combinations of ultrasonication, hot water, and ligninolytic enzyme (e.g. Prima Green Eco Fade LT 100) or other enzymes during pretreatment to improve lignocellulosic conversion efficiency to sugars, as this research pretreatment procedure was enzyme-free.
- Study use of transgenic strains (e.g. *S. cerevisiae* L2612δGC) or other microbes to improve overall ethanol yield directly from both cellulose and hemicellulose.

- Investigate naturally occurring microbes or cheaper options for enzymes for biological conversion route, since enzymes accounted for the major cost (29−45%) of biological conversion.
- Combine biological and thermal conversions to use the lignin or any residue that was not consumed by biological conversion processes. Such an integrated process may improve energy and cost effectiveness of the complete process.
- Determine product-composition variations, and quality from pyrolysis of the individual structures (cellulose, hemicellulose and lignin) of the biomass.
- Improve upgraded product yield by increasing the distillate (light fraction) volume by collecting fraction up to 200 ^{o}C during distillation. This work investigated the fraction up to 140 ^{o}C.
- Study the heavier fraction of bio-oil; apply a similar processing route to the heavier fraction, crack the oil for heat generation, extract phenol from the heavier fraction (phenol-rich), and obtain another high-value product.
- Test the upgraded product (switchgrass gasoline) using other gasoline standard tests: (i) Standard specification for automotive spark-ignition engine fuel (ASTM D 4814); (ii) Gasoline vapor pressure (ASTM D 5191); (iii) Gum content (ASTM D 381); and (iv) Bromine number (ASTM D1159).
- Perform more detailed cost analyses on the biological and thermal conversion processes.

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