HYDROTHERMAL GASIFICATION OF FLAX STRAW IN SUBCRITICAL WATER

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Submitted to the Faculty of Graduate Studies and Research
In Partial Fulfillment of the Requirements
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In
Process Systems Engineering
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By
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Inibehe Ntiedo Harry, candidate for the degree of Master of Applied Science in Process Systems Engineering, has presented a thesis titled, *Hydrothermal Gasification of Flax Straw in Subcritical Water*, in an oral examination held on December 19, 2012. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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ABSTRACT

There is substantial interest in the application of biomass as a source for renewable fuels and chemicals. When processed for energy purposes, biomass has the benefit of being either CO$_2$ neutral or a sink. Flax straw, which is rich in lignin content, decays slowly, making it difficult to incorporate it into the soil. Flax straw can be gasified to produce fuel gases or liquid fuels. However, flax straw may contain a higher percentage of water, causing high drying cost if a conventional gas-phase conversion process is employed. This can be avoided if gasification in subcritical or supercritical water is employed. Subcritical water gasification provides a nice alternative to produce chemical intermediates from biomass due to the unique properties of water in that regime.

In this study, a 600 mL high pressure autoclave was used to study the effect of reaction temperature, pressure, flax straw concentration, and retention time on the product distribution and conversion of flax straw under subcritical hydrothermal gasification. The objective was to optimize a plausible process of biomass gasification under subcritical water conditions. The gaseous products, analysed by online GC, were CO$_2$, CO, H$_2$, traces of CH$_4$, and C$_2$H$_6$. The liquid products analysed using gas chromatography/mass spectrometry (GC/MS) were furfural, phenol, acetic acid, and formic acid. The results show that the product yields are sensitive to the reaction parameters such as temperature, pressure, and retention time. Furfural, a key compound in the liquid phase, was chosen for its industrial application as a product of interest, and
its yield was optimized by using two different kinds of acid catalysts (H-ZSM-5 and HCl). Both catalysts showed good catalytic activity and selectivity towards furfural.

A kinetic study for flax straw degradation was also performed at three designated temperatures (225, 275, and 325°C) using the carbon conversion results obtained from the ultimate analysis. A highest carbon conversion of about 40% was achieved at 325°C. The experimental results were used to derive an empirical rate model. The model was of the form 

$$-r_A = \frac{dX_A}{dt} = 8.3156 \times 10^{-1} e^{-27969.63/RT}(1 - X_A)^2$$

activation energy (Ea) was found to be 27,969.6 J/mol, and the order of the reaction (n) was 2. Estimation of the values of the model parameters was based on the minimization of the sum of the residual squares of the reaction rates using the Gauss-Newton and Levenberg-Marquardt algorithm with non-linear regression (NLREG) software. Good agreement between the experimental and predicted rate was obtained with an absolute average deviation (AAD) of 8.4%.
ACKNOWLEDGEMENTS

First and foremost, I want to thank the almighty God for giving me the strength and wisdom to complete this thesis work. May his name be praise.

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TABLE OF CONTENTS

ABSTRACT i

ACKNOWLEDGEMENTS iii

TABLE OF CONTENTS iv - ix

LIST OF TABLES x

LIST OF FIGURES xi

LIST OF APPENDICES xiv

NOMENCLATURE xv

CHAPTER 1: INTRODUCTION 1

1.1 BIOMASS AND SUSTAINABLE ENERGY 1

1.2 BIOMASS CONVERSION TECHNOLOGIES 3

1.3 PROBLEM IDENTIFICATION AND RATIONALE 7

1.4 RESEARCH OBJECTIVES 9

CHAPTER 2: LITERATURE REVIEW 11

2.1 HYDROTHERMAL GASIFICATION 11
2.2 SUBCRITICAL AND SUPERCRITICAL WATER

2.2.1 Super critical Water

2.2.2 Subcritical Water

2.3 KEY PROPERTIES OF SUBCRITICAL WATER FOR HYDROTHERMAL GASIFICATION OF BIOMASS

2.3.1 Ionic Strength and pH

2.3.2 Dielectric Constant

2.3.3 Viscosity and mass Transfer

2.4 PRODUCTS OF HYDROTHERMAL GASIFICATION IN SUB/SUPERCRITICAL WATER

2.5 USES OF SOME CHEMICAL COMPOUNDS PRESENT IN THE LIQUID PRODUCT

2.5.1 Formic Acid

2.5.2 Acetic Acid

2.5.3 5-Hydromethyl Furfural (5-HMF)

2.5.4 Other Important Liquid Products

2.6 FURFURAL AS A VITAL CHEMICAL FOR THE INDUSTRY
CHAPTER 3: EXPERIMENTAL PROCEDURES

3.1 PRECIS

3.2 CHEMICALS, GASES, AND EQUIPMENT

3.2.1 Chemicals

3.2.2 Gases

3.2.3 Equipment

3.3 FEED MATERIALS AND PREPARATION

3.4 CATALYST USED

3.4.1 Mineral Acid Catalyst

3.4.2 Solid Acid Catalyst

3.5 REACTION FEED STOCK

3.6 OPERATING CONDITIONS

3.7 EXPERIMENTAL SETUP AND PROCEDURE

3.7.1 Schematic and Description of Experimental Setup

3.7.2 Typical Experimental Run
3.8 PRODUCTS ANALYSIS

3.8.1 Gaseous Products Analysis

3.8.2 Liquid Products Analysis

3.9 EQUATIONS USED TO CALCULATE YIELD AND CONVERSION

CHAPTER 4: RESULTS AND DISCUSSION

4.1 LIQUID PRODUCT COLOUR TRANSFORMATION

4.2 QUALITATIVE AND QUANTITATIVE ANALYSIS OF THE LIQUID PRODUCTS

4.3 QUALITATIVE AND QUANTITATIVE ANALYSIS OF THE GASEOUS PRODUCTS

4.4 EFFECT OF PROCESS PARAMETERS ON THE LIQUID PRODUCT YIELD

4.4.1 Effect of temperature

4.4.2 Effect of retention time

4.4.3 Effect of feed concentration

4.4.4 Effect of pressure
4.5 EFFECT OF PROCESS PARAMETERS ON THE GAS PRODUCT YIELD

4.5.1 Effect of temperature

4.5.2 Effect of retention time

4.6 OPTIMIZING THE YEILD OF FURFURAL

4.6.1 Determination of Optimum Temperature

For Furfural Yield

4.6.2 Acid Catalysed Reaction

4.6.2.1 Effect of Acidity (pH) on Furfural Yield

4.6.2.2 Effect of Solid Acid Catalyst on Furfural Yield

4.6.2.3 Comparing the Activity of Both Catalysts

4.7 EFFECT OF H-ZSM-5 CATALYST ON THE GAS YIELD

4.8 KINETIC STUDIES

4.8.1 Empirical Rate Model

4.8.2 Experimental Rate of Reaction

4.8.3 Estimation of Parameters of Rate Model
CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS  

5.1 CONCLUSIONS  

5.2 RECOMMENDATIONS  

REFERENCES  

APPENDICES
## LIST OF TABLES

| Table 1.1 | Moisture content of selected biomass | 4 |
| Table 1.2 | Energy efficiency for different biomass conversion processes | 5 |
| Table 2.1 | Physical properties of water at the different temperature regions | 19 |
| Table 2.2 | Content of the aqueous liquid phase | 24 |
| Table 3.1 | Flax straw ultimate analysis results | 34 |
| Table 3.2 | Characteristic properties of H-ZSM-5 | 35 |
| Table 4.1 | GC-MS results of detected compounds in the liquid phase | 50 |
| Table 4.2 | Experimental kinetic data table | 88 |
| Table 4.3 | Estimated parameters of the rate model | 90 |
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2.1</td>
<td>Phase diagram of water showing supercritical region</td>
<td>15</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Phase diagram of water showing subcritical region</td>
<td>18</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>Reaction pathway for cellulose decomposition in supercritical region</td>
<td>25</td>
</tr>
<tr>
<td>Figure 2.4</td>
<td>Dehydration of pentose from hemicelluloses to furfural</td>
<td>29</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>Schematic diagram of experimental setup used for the process</td>
<td>38</td>
</tr>
<tr>
<td>Figure 4.1</td>
<td>Appearance of liquid phase at the end of the reaction at various temperatures</td>
<td>46</td>
</tr>
<tr>
<td>Figure 4.2</td>
<td>GC-MS chromatogram of the liquid product formed</td>
<td>49</td>
</tr>
<tr>
<td>Figure 4.3</td>
<td>Effect of the Reaction temperature on the liquid product yield at 0 min retention time, initial reactor gauge pressure of 0 bar, and 5 wt% of flax straw</td>
<td>54</td>
</tr>
<tr>
<td>Figure 4.4</td>
<td>Effect of reaction temperature on the liquid product yield at 0 min retention time, initial reactor gauge pressure of 0 bar, and 10 wt% of flax straw</td>
<td>55</td>
</tr>
<tr>
<td>Figure 4.5</td>
<td>Effect of retention time on the liquid product yield at 225°C, initial reactor gauge pressure of 0 bar, and (a) 5 wt% flax straw, (b) 10 wt% flax straw</td>
<td>58</td>
</tr>
</tbody>
</table>
Figure 4.6  Effect of retention time on the liquid product yield at 275°C, initial reactor gauge pressure of 0 bar and (a) 5 wt% flax straw, (b) 10 wt% flax straw

Figure 4.7  Effect of retention time on the liquid product yield at 325°C, initial reactor gauge pressure of 0 bar, and (a) 5 wt% flax straw, (b) 10 wt% flax straw

Figure 4.8  Effect of feed concentration on the liquid product yield at 225°C, retention time, and initial reactor gauge pressure of 0 bar

Figure 4.9  Effect of pressure on the liquid product yield at 225°C, 0 min retention time, and 5 wt%

Figure 4.10 Effect of reaction temperature on the gas yield at 0 min retention time, initial reactor gauge pressure of 0 bar, and 10 wt% of flax straw

Figure 4.11  Effect of retention time on the liquid product yield at 225°C, initial reactor gauge pressure of 0 bar, and 10 wt% flax straw

Figure 4.12  Effect of retention time on the liquid product yield at 275°C, initial reactor gauge pressure of 0 bar, and 10 wt% flax straw

Figure 4.13  Effect of retention time on the liquid product yield at 325°C, initial reactor gauge pressure of 0 bar, and 10 wt% flax straw
Figure 4.14  Determination of optimum temperature for furfural yield using 5 wt% of flax straw, 0 min retention time, and initial reactor gauge pressure of 0 bar

Figure 4.15  Mechanism of pentose dehydration to furfural

Figure 4.16  Effect of acidity of furfural yield at 250°C, initial reactor gauge pressure of 40 bar, and 5 wt% flax straw

Figure 4.17  Effect of H-ZSM-5 on furfural yield at 250°C, initial reactor gauge pressure of 0 bar, and 5 wt% flax straw

Figure 4.18: Acid catalysed reaction pathway for flax straw gasification in sub critical water

Figure 4.19  Effect of H-ZSM-5 on the gas yield at 325°C, initial reactor gauge pressure of 0 bar, 10 wt% flax straw, and 0 min retention time

Figure 4.20  Carbon conversions for at different retention time for temperatures of 225, 275, and 325°C

Figure 4.21  Parity plot of experimental vs. predicted rate
<table>
<thead>
<tr>
<th>APPENDIX A:</th>
<th>Calculation for yield and conversion</th>
<th>103</th>
</tr>
</thead>
<tbody>
<tr>
<td>APPENDIX B:</td>
<td>Curve fitting calculation and experimental rate calculation</td>
<td>108</td>
</tr>
<tr>
<td>APPENDIX C:</td>
<td>NLREG code with results for empirical rate model</td>
<td>112</td>
</tr>
</tbody>
</table>
NOMENCLATURE

Notation

5-HMF  5-Hydromethyl Furfural

%  Percent

° C  Degree Celsius

K  Degree Kelvin

A  Pre-exponential factor or collision factor

AAD  Average Absolute Deviation

atm  Atmosphere

bar  Unit of pressure

CH₄  Methane

CH₁₅O₀.₆₂  Flax straw

C₂H₅  Ethane

CH₃CO₂H  Acetic acid

C₅H₄O₂  Furfural

C₆H₅OH  Phenol

C₆H₁₂O₆  Glucose
C_{6}H_{10}O_{5}  \quad \text{Cellulose}

Ca  \quad \text{Calcium}

CHNS  \quad \text{Carbon-Hydrogen-Nitrogen-Sulphur}

CO  \quad \text{Carbon Monoxide}

CO_{2}  \quad \text{Carbon Dioxide}

E_{a}  \quad \text{Activation Energy}

g  \quad \text{Gram}

GC  \quad \text{Gas Chromatogram}

GC/MS  \quad \text{Gas Chromatogram/Mass Spectroscopy}

H^{+}  \quad \text{Hydrogen ion}

h  \quad \text{hour}

HCl  \quad \text{Hydrochloric acid}

HCOOH  \quad \text{Formic acid}

HPLC  \quad \text{High Performance Liquid Chromatography}

H-ZSM-5  \quad \text{Zeolite catalyst}

H_{2}O  \quad \text{Water}

H_{2}SO_{4}  \quad \text{Sulfuric acid}
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Term</th>
</tr>
</thead>
<tbody>
<tr>
<td>i.d</td>
<td>Internal diameter</td>
</tr>
<tr>
<td>J</td>
<td>Joule</td>
</tr>
<tr>
<td>k</td>
<td>Rate constant</td>
</tr>
<tr>
<td>(K_2\text{CO}_3)</td>
<td>Potassium carbonate</td>
</tr>
<tr>
<td>mg</td>
<td>Milligram</td>
</tr>
<tr>
<td>Mg</td>
<td>Magnesium</td>
</tr>
<tr>
<td>min</td>
<td>Minutes</td>
</tr>
<tr>
<td>mL</td>
<td>Millilitre</td>
</tr>
<tr>
<td>mm</td>
<td>Millimetre</td>
</tr>
<tr>
<td>MPa</td>
<td>Mega Pascal</td>
</tr>
<tr>
<td>n</td>
<td>Reaction order</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>NLREG</td>
<td>Non-Linear Regression</td>
</tr>
<tr>
<td>(\text{O}_2)</td>
<td>Oxygen</td>
</tr>
<tr>
<td>(\text{OH}^-)</td>
<td>Hydroxide ion</td>
</tr>
<tr>
<td>P</td>
<td>Pressure</td>
</tr>
<tr>
<td>pH</td>
<td>Negative Logarithm of Hydrogen Ion Concentration</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>psi</td>
<td>Pounds per square inch</td>
</tr>
<tr>
<td>R</td>
<td>Molar gas constant (8.314 J/mol/K)</td>
</tr>
<tr>
<td>RT</td>
<td>Retention time</td>
</tr>
<tr>
<td>sec</td>
<td>Second</td>
</tr>
<tr>
<td>t</td>
<td>Reaction time</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal Conductivity Detector</td>
</tr>
<tr>
<td>UHP</td>
<td>Ultra High Purity</td>
</tr>
<tr>
<td>$W_{Ci}$</td>
<td>Initial weight of carbon in flax straw</td>
</tr>
<tr>
<td>$W_C$</td>
<td>Weight of carbon in the char at temperature (T) and time (t)</td>
</tr>
<tr>
<td>w%</td>
<td>Weight Percent</td>
</tr>
<tr>
<td>$X_A$</td>
<td>Flax Straw Conversion</td>
</tr>
<tr>
<td>$X_C$</td>
<td>Carbon Conversion</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 BIOMASS AND SUSTAINABLE ENERGY

Biomass can be defined as organic materials, originating from plants, which contain stored energy from sunlight through the process of photosynthesis. The chemical reaction taking place during the photosynthesis is represented in the equation below:

\[ 6\text{CO}_2 + 12\text{H}_2\text{O} \xrightarrow{\text{sunlight}} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 + 6\text{H}_2\text{O} \quad (1.1) \]

The energy contained in the plants is transferred to humans and animals through the food chain. The same chemical energy is also available in industrial and agricultural waste, house hold garbage, and municipal sewage (Chowdhury et al., 2010), which gives an excellent opportunity for researchers to devise novel process systems to harness the remnant chemical energy available in the above resources to generate valuable commodities such as fuels and chemicals.

The disposal of hazardous industrial and agricultural biomass wastes, which are generated from feedlots and food processing operations, has drawn global concern in the areas of health and environment. The key sources of biomass are forest and agricultural biomass, food processing residues, forest residues, industrial wastes,
household garbage, and municipal wastes. Researchers have found that direct application of livestock manure for soil amendment results in the contamination of the surface and ground water and also emission of methane and nitrous oxide (Chowdhury et al., 2010). In Canada, the promulgation of the Nutrient Management Act jointly by OMAFRA and the Ontario Ministry of Environment (MEO) has limited the availability of land for the disposal of agricultural and municipal wastes (Guo et al., 2007). As a result of this act, there is an increase in the disposal costs, which may also hinder industrial growth.

Conversion of this abundant waste and lignocellulosic biomass into valuable chemicals and biofuels could be a breakthrough in solving this challenging problem of treating the hazardous waste streams that are polluting the environment while at the same time making way for newer energy resources. It is well known that using fossil fuels such as crude oil and coal causes anthropogenic CO$_2$ emissions, which are responsible for global warming (Yat et al., 2008). The conversion of this abundant biomass to biofuels and transportation fuels not only provides a viable option to improve energy security, but also reduces greenhouse gas emissions (Parveen et al., 2009). Therefore, there has been an immense push globally to develop realistic, environmentally friendly, and economic solutions to replace conventional fuels with biofuels. Biofuels are considered cleaner compared to fossil fuels, as their carbon content is part of the natural carbon cycle (Knežević et al., 2006). Due to the short carbon cycle of biomass (biofuels), its net contribution to CO$_2$ build up in the atmosphere is negligible (Knežević et al., 2006). In the literature, it has been reported that cellulosic ethanol and ethanol produced from other biomass
resources has the ability to reduce the greenhouse gas emissions by 86%. Also lignocellulosic materials such as agricultural waste residue (wheat straw, corn stover, sugarcane, etc.), forest products (soft and hard wood), as well as dedicated crops, are biomass renewable resources for energy. Also, biomass can be used for electricity generation via gasification in conventional coal-fired power stations.

Of course, on one hand, there is an immense potential in the biomass-based feedstocks waiting to be explored, but on the other hand, biomass feedstocks are known to possess low calorific value, low energy density, and high moisture, which makes them unsuitable for any conventional thermochemical processes such as gasification, pyrolysis, etc. The high moisture in the biomass drastically reduces the energy efficiency of the process on account of the need for drying prior to use.

The water content in agricultural waste may be up to 95%, and it is approximately 80% in municipal waste and 20% in dry solid waste, in which 75% of this solid waste is organic matter (Gasafi et al., 2007). This research is focused on solving the problem associated with wet biomass by choosing a suitable technology as well as operating conditions for converting the wet biomass into valuable chemicals.

1.2 BIOMASS CONVERSION TECHNOLOGY

As discussed in the previous section, one of the major problems of biomass is its high moisture content. Table 1.1 below shows the moisture content of various commonly occurring biomass and associated wastes. Table 1.2 compares the energy conversion efficiency of various processes existing today to convert wet biomass to value added products.
Table 1.1: Moisture content of selected biomass (Basu et al., 2009)

<table>
<thead>
<tr>
<th>BIOMASS TYPE</th>
<th>MOISTURE (% Wet basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat straw</td>
<td>8-20</td>
</tr>
<tr>
<td>Sawdust</td>
<td>25-55</td>
</tr>
<tr>
<td>RDF pellet</td>
<td>25-35</td>
</tr>
<tr>
<td>Wood bark</td>
<td>30-60</td>
</tr>
<tr>
<td>Corn Stalk</td>
<td>40-60</td>
</tr>
<tr>
<td>Rice Straw</td>
<td>50-80</td>
</tr>
<tr>
<td>Food waste</td>
<td>70</td>
</tr>
<tr>
<td>Cattle manure</td>
<td>88</td>
</tr>
<tr>
<td>Water hyacinth</td>
<td>95.3</td>
</tr>
</tbody>
</table>
**Table 1.2:** Energy efficiency for different biomass conversion processes (Yoshida et al., 2003)

<table>
<thead>
<tr>
<th>Moisture content in feed</th>
<th>5%</th>
<th>31%</th>
<th>55%</th>
<th>75%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass conversion process</td>
<td>Energy conversion efficiency (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal gasification</td>
<td>61</td>
<td>55</td>
<td>47</td>
<td>27</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>57</td>
<td>53</td>
<td>45</td>
<td>27</td>
</tr>
<tr>
<td>Liquefaction</td>
<td>39</td>
<td>37</td>
<td>36</td>
<td>34</td>
</tr>
<tr>
<td>Anaerobic digestion</td>
<td>31</td>
<td>31</td>
<td>31</td>
<td>31</td>
</tr>
<tr>
<td>Sub/Supercritical water</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>55</td>
</tr>
</tbody>
</table>
From Table 1.2, it can be noted that the energy conversion efficiency decreases as the moisture content in the feed increases. This is primarily due to the increasing amount of energy consumed during the drying process. In thermal gasification conversion, lignocellulosic feedstocks such as wood and forest products are broken down using heat to synthesis gas, primarily carbon monoxide and hydrogen. The feedstock is usually partially oxidized, or reformed with a gasifying agent (air, oxygen, or steam), which produces synthesis gas (syngas). The makeup of syngas will vary depending on the type of feedstock, their moisture content, the type of gasifier used, the gasification agent, and the temperature and pressure in the gasifier. In pyrolysis processing, biomass feedstocks are broken down using heat in the absence of oxygen, to produce a bio-oil that can be further refined to a hydrocarbon product. The decomposition occurs at lower temperatures than thermal gasification processes, and produces liquid oil instead of a synthesis gas. Oil produced varies in oxygen content or viscosity according to the feedstock used. On the other hand, anaerobic digestion refers to the process whereby microorganisms convert chemical energy in solid biomass material into an energy carrier, often with high efficiency relative to thermochemical conversion. The products are usually a mixture of methane and CO\textsubscript{2} in almost equal proportions. These microorganisms have the flexibility to process waste streams as well as biomass feedstock from residues and energy crops. Hydrothermal liquefaction is generally carried out at 280–370 °C and between 10 and 25 MPa. Under these conditions, water is still in the liquid state, but exhibits a range of exotic properties. This water is referred to as sub-critical water. The main products are bio-crude with a relatively high heating value, char, water-soluble substances and gas. Supercritical water gasification, on the other hand,
converts the wet biomass into gases and has a higher energy conversion efficiency of wet biomass to gases compared to the rest of the processes.

Biomass gasification in sub/supercritical water offers an attractive choice to eliminate the energy intensive drying process, especially when the moisture content is above 30% (Savage et al., 2009). Compared to other biomass thermochemical processes, sub/supercritical water has high gasification efficiency and can operate at a lower temperature, especially in the subcritical regime (Lu et al., 2006). One great benefit of this process is that since the solvent is water, the thermal efficiency of the process is in no way affected by biomass humidity. Further detailed discussion on the subject of subcritical and supercritical water gasification can be found in Chapter Two of this thesis.

The next section defines the problems faced by Canadian farmers in general and Saskatchewan farmers in particular, which is the main source of motivation behind the current research project.

1.3 PROBLEM DEFINITION AND MOTIVATION

Flax straw, a biomass, is the fibrous stalk of the flax plant that is left in the field after the flax seed has been removed during combining (Agriculture and Agric-Food Canada, 2011). Unlike straw of other crops that is commonly grown in the grassland, flax straw has been reported to have a long history of being used rather than tilled into the soil, primarily because of its strong fibre content. Flax was first introduced in Canada in 1617 (Agriculture and Agric-Food Canada, 2011), and the country is the largest grower and exporter of flax in the world. Saskatchewan is a prairie province and has an economy base significantly on agriculture (Tusher et al., 2010). It is reported that 70% of the total
flax production in Canada comes from Saskatchewan (Comeau, 2006). This flax plant is an excellent crop for the grassland because it matures even under cool weather conditions and also has a short growing season (Agriculture and Agric-Food Canada, 2011).

The problem of flax to farmers is that the tough stem fibres in flax straw decay slowly, creating a difficult condition of incorporating the straw into the soil after harvest since the fibres wrap themselves around and/or plug disks, wheels, and shovels (Tusher et al., 2010). As a result of this, farmers traditionally manage flax straw by sinking it in windrows behind the combine or burning it after raking it into piles. Recently, straw chopper spreaders have been used by farmers to effectively chop the flax straw and spray it across the field. However, using this abundant flax straw, it is possible to generate renewable fuels and/or chemicals via a sub/supercritical water gasification process, which will not only address this problem faced by farmers but also serve as a renewable energy source capable of replacing the current fossil fuel. Flax straw as a renewable biomass resource has the prospect to serve as a sustainable supply of chemical intermediates (e.g., alcohols, aldehydes, furfural, acids, etc.) and fuels. The challenge faced by many researchers is always how to develop a cost effective processing methods/process for converting such highly functionalized carbohydrate moieties into value-added chemicals (Juben et al., 2007). Also, furfural and its derivatives can be produced from flax straw by acid-catalysed dehydration of the pentoses and hexoses contained in the flax straw (Huber et al., 2006).

Furfural is a vital chemical used for the commercial production of furan. It is also used in the refining of lubricating oil and, in condensation with phenol, formaldehyde, acetone, or urea, yields resins with excellent thermostatic properties and extreme physical
strength (McKillip, 1981). Furfural can also serve as a precursor for production of liquid alkanes (C\textsubscript{7}-C\textsubscript{15}) that serve as components for diesel fuel (Huber et al., 2006).

This current research aims at identifying the optimal reaction conditions to achieve high yields of furfural from flax straw.

1.4 **RESEARCH OBJECTIVES**

The overall goal of this research was to optimize a possible process of flax straw gasification in subcritical water to achieve a high yield of a selected product of interest (furfural) by varying the operating parameters and process conditions.

The objectives are listed as follows:

- To conduct experiments in the subcritical water gasification regime using flax straw in subcritical conditions of water (< 374°C and 22 MPa) using flax straw and analyse the liquid and gaseous products qualitatively and quantitatively.
- Study the effect of process parameters such temperature, pressure, concentration, and retention time on the yield of the gaseous product and four key compounds (formic acid, acetic acid, furfural, and phenol) in the liquid product.
- Determine the optimum condition to achieve the highest gas yield and liquid product yield.
- Optimize the process to achieve a high yield of furfural by adding a catalyst.
- Study the effect of acidity and solid acid catalyst on the furfural yield.
- Compare the activity of homogeneous and heterogeneous acid catalyst on furfural yield.
- Kinetic study of flax straw conversion in subcritical water in order to establish an empirical rate expression for the process.
CHAPTER 2

LITERATURE REVIEW

2.1 HYDROTHERMAL GASIFICATION

Hydrothermal gasification of biomass can be defined as a thermochemical technique that uses liquid water in its subcritical or supercritical state as a reaction medium for converting wet biomass to gases and useful liquid compounds (Knezevic et al., 2006). Andrew et al. (2008) also defines the hydrothermal process as a technology for converting biomass into liquid and gaseous fuels in hydrothermal media. For the hydrothermal conversion of biomass, a lot of terms are used in the literature, such as hydrothermal degradation, hydrothermal decomposition, hydrothermal upgrading, and hydrothermolysis (Jin et al., 2008; Goto et al., 2004; Kabyemela et al., 1997; Bobleter et al., 1976) etc.

Temperature plays a vital role in determining the amount and nature of end products formed during the course of hydrothermal gasification. Generally, solid, liquid, and gaseous products are produced at all temperatures. It is reported that the extent of the respective primary product formation shifts from solid (at low temperature) via liquid (at medium temperature) to gaseous product (at high temperature) (Maria et al., 2011). As a result of this, at a temperature below 200ºC, the main products are solid chars/carbon. Between temperatures of 200ºC and 300ºC, the main product is liquid; this process is also known as hydrothermal liquefaction. Gas product formation dominates at a temperature above 375ºC. Hydrothermal processing offers numerous possible advantages over other
biofuel production methods. Such advantages include high throughputs, good separation efficiency, and the ability to use mixed feedstocks like lignocelluloses materials and waste (Andrew et al., 2008). In addition, due to the high temperature of the process, the biofuels produced are free from biologically active organisms, including viruses and bacteria (Andrew et al., 2008). In order to really understand this process, it is important to take a quick look at the unique physico-chemical properties of the two different kinds of water (subcritical and supercritical), which forms the medium of gasification in these processes.

2.2 SUBCRITICAL AND SUPERCRITICAL WATER

From an engineering point of view, subcritical and supercritical water have drawn much attention in many years as a potential chemical medium with numerous applications, such as supercritical water oxidation of aqueous organic waste (Dinaro et al., 2000), subcritical water extraction, and hydrolysis of organic compounds (Kubatova et al., 2011). Yoshida et al. (2004, 1999) reported that subcritical water hydrolysis is an efficient method for the production of useful chemicals from food wastes and other food-related substances. Attention has been drawn recently to the hydrolysis and decomposition of biomass in subcritical or supercritical water for industrial synthesis of industrial chemical related materials (Oomori et al., 2004; Minowa et al., 1999; Moreschi et al., 2004; Fleche et al., 1982; Antal et al., 1988, 1990). Also, a lot of attention has been given to converting saccharides into valuable products with numerous industrial applications. Fleche and Gaset (1982) reported in their patented work that some investigators have performed dehydration of saccharides into 5-hydromethyl furfural in subcritical water (Antal et al., 1988, 1990; Bicker et al., 2003). Because of this, many
scientists prefer water to traditional toxic organic solvent for chemical reactions. Water in its critical state has properties different from water under normal conditions. The following sections will detail the meaning and difference between the two kinds of water (supercritical and subcritical water).

2.2.1 SUPERCRITICAL WATER

According to Chowdhury et al. (2010), a supercritical fluid is defined as a substance at a temperature and pressure above its critical point. Figure 2.1, adopted from Chowdhury et al. (2010), shows the phase diagram of water, and a lot of information can be drawn from it. The critical point in the diagram shows the condition at which a phase boundary ceases to exist. Across the equilibrium line, the pressure and temperature increase and the liquid density decreases while the vapour density increases until both reach the critical point. Above that point, the fluid becomes a single supercritical phase with properties in between gas and liquid (Chowdhury et al., 2010). The critical point of water is at a temperature of 374°C and a pressure of 22 MPa (Wagner, 2002). As such, water at a temperature and pressure above this point are referred to as “supercritical water.”

The properties of water at this condition undergo dramatic changes. An important property of supercritical water is that there exists almost no mass transfer limitation, implying that the high diffusivity of water (with diffusion coefficient that is 100 times higher than ambient water) can significantly enhance mass transfer (Ding et al., 1996). Also, supercritical water acts as a non-polar dense gas that has a solvation property similar to those of low polarity organic solvent. As a result of this, hydrocarbons and
gases (e.g., CO₂, N₂, O₂, etc.) are highly soluble and are completely miscible under typical operating conditions (Chowdhury et al., 2010). Knezevic et al. (2006), reported in his work that the lower solubility of ions and lower activity of H⁺ and OH⁻ cause the reaction at high temperature to proceed through free radical pathways instead of ionic pathways. As a result of the higher diffusion constant and lower viscosity of supercritical water, mass transfer limitation to a greater extent is lower than that of liquid water. Even for a catalytic process, pore diffusion limitation can be overcome under supercritical water (Chowdhury et al., 2010).
Figure 2.1: Phase diagram of water showing supercritical region (Chowdhury et al. 2010)
2.2.2 SUBCRITICAL WATER

The terminologies used to describe water under subcritical conditions in biomass processing are widely varied. The most general term is hot compressed water (HCW), as reported by Yu et al. (2008), which describe temperature above 150ºC and at various pressures above atmospheric pressure. Many definitions are found in the literature for subcritical water. Krammer et al. (2000) defines subcritical water as water at T < 370ºC and 0.4<P< 22MPa. Srokol et al. (2004) reported 300 ≤ T ≥ 350ºC and at 10 ≤ P ≤18MPa. In addition, the term high-temperature water (HTC) is defined broadly by Akiya et al. (2002) as liquid water above 200ºC. The above definition originated from the usual reaction conditions of hydrothermal biomass conversion and do not exactly define the term “subcritical water.” Basically, subcritical water is not a physically defined state, since all water below the critical point and higher than the triple point is either liquid or gaseous. This is shown clearly in Figure 2.2, adapted from Maria et al. (2011).

The term subcritical water is introduced to distinguish water conditions below the critical point. As reported by Cheng et al. (2010) and Soto et al. (2001), the most practical definition that takes into account those of hot compressed water and pressurized hot water (Cheng et al., 2010; Soto et al., 2001; Mok et al., 1992; Minowa et al., 1998) denotes water above its boiling point and ambient pressure (>100ºC and 0.1MPa) and below its critical point of 374ºC at 22.1 MPa (Frimmel et al., 2003). With respect to Figure 2.2, the chemistry of water at this temperature regime differs significantly. Apart from the temperature effects, it is the change in the major chemical and physical properties of water that decisively influences its properties as a solvent. Table 2.1,
adapted from Maria et al. (2011), compares the major physical properties of water in the different temperature regions.
**Figure 2.2:** Phase diagram of water showing subcritical region (Maria et al., 2011)
<table>
<thead>
<tr>
<th></th>
<th>Ambient Temperature</th>
<th>Subcritical water</th>
<th>Supercritical water</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature [°C]</strong></td>
<td>0-100</td>
<td>100-374</td>
<td>&gt;374</td>
</tr>
<tr>
<td><strong>Vapour Pressure [MPa]</strong></td>
<td>0.003 (24°C)</td>
<td>0.1 (100 8 C)–22.1 (374 8C)</td>
<td>&gt;22.1</td>
</tr>
<tr>
<td><strong>Aggregate state</strong></td>
<td>liquid</td>
<td>liquid</td>
<td>No phase</td>
</tr>
<tr>
<td><strong>Viscosity [μPas]</strong></td>
<td>L:884 G:9.9 (25°C)</td>
<td>L:277 G:12.3(101°C) L:50.4 G: 30.7(371°C)</td>
<td>low</td>
</tr>
<tr>
<td><strong>Density [g/cm³]</strong></td>
<td>0.997 (25°C)</td>
<td>0.958 (101°C .0.11MPa) 0.692(330°C, 30MPa)</td>
<td>Between gas-like and liquid-like density.</td>
</tr>
<tr>
<td><strong>Heat Capacity C_p [Jg⁻¹K⁻¹]</strong></td>
<td>L: 4.2 G :2.0(25°C)</td>
<td>L:4.2 G:2.2 (101°C) L:69 G:145 (371°C)</td>
<td>1300 (400°C, 25MPa)</td>
</tr>
<tr>
<td><strong>Dielectric Constant</strong></td>
<td>78.5(25°C, 0.1MPa)</td>
<td>27.1(250°C, 5MPa) 18.2(330°C, 30MPa)</td>
<td>5.9 (400°C, 25MPa) 10.5(400°C, 50MPa)</td>
</tr>
<tr>
<td><strong>Compressibility</strong></td>
<td>no</td>
<td>Slightly increased, but still a liquid ( at 370°C)</td>
<td>yes</td>
</tr>
<tr>
<td><strong>Ion product K_w [mol²L⁻²]</strong></td>
<td>10⁻¹⁴ (increases to 10⁻¹² at 100°C)</td>
<td>Increases from 10⁻¹² (100°C) to 10⁻¹¹ (300°C)</td>
<td>Strongly decreases to below 10⁻²⁰ (400°C) and below 10⁻²³(550°C)</td>
</tr>
</tbody>
</table>
2.3 KEY PROPERTIES OF SUBCRITICAL WATER FOR HYDROTHERMAL GASIFICATION OF BIOMASS

This section explains in detail the key properties of subcritical water, which makes it a suitable reaction medium for this study. We should understand that the chemical reaction occurring in an aqueous media is closely related to the properties of the solvent, in this case, water. These properties are:

2.3.1 Ionic Strength and pH

With increasing temperature, the ion product of water ($K_w$) increases by three orders of magnitude from $K_w = 10^{-14}\text{mol}^2\text{L}^{-2}$ at 25°C to $K_w \approx 10^{11}\text{mol}^2\text{L}^{-2}$ at 300°C (Maria et al., 2011). Above this temperature, the $K_w$ decreases further; close to the supercritical point, the decrease is very sharp and results in a value below $10^{-20}\text{mol}^2\text{L}^{-2}$ at 380°C (Broll et al., 1999; Marshall et al., 1980; Xu et al., 1990). From this, it can be deduced that in subcritical water, all ionic reactions involving water molecules as reacting agents are generally enhanced (Maria et al., 2011). An example is in the hydrolysis of cellobioses to their respective monomers as reported by Goto et al. (2004) and Kabyemela et al. (1997). In addition, the stabilization of the charged transition state triggers the ionic reactions, and as a result of this, the catalytic effect of the addition of acids and/or bases in subcritical water biomass gasification processes enhances the proton/hydroxide ion concentration, as well increases the ionic strength (Maria et al., 2011).
2.3.2 Dielectric Constant

As a result of the lower number of ordered hydrogen bonds per water molecule, the relative dielectric constant of water decreases with temperature, as shown in Table 2.1. According to Weingartner et al. (2005), with increasing temperature, the solubility of the ionic molecules strongly decreases, whereas that of hydrophobic molecules increases. This observable fact can be used for extraction processes (Akiya et al., 2002), as well as for easier phase separation of organic and polar reaction products after cooling of the reaction solution. In summary, the decreased relative electric permittivity and increased ion product of subcritical water enhances the preference of several chemical reactions such as:

- Reaction involving water as the reactant (hydrolysis); an example is the hydrolysis of cellobiose in subcritical water (Akiya et al., 2002).
- Polar transition state reactions; an example being nucleophilic substitution and elimination reactions (Akiya et al., 2002; Xu et al., 1990; Kuhlmann et al., 1994).

The reaction rates of the above-mentioned reactions are found to increase in subcritical water.

2.3.3 Viscosity and mass transfer

From Table 2.1, one can note that the viscosity of water decreases sharply with temperature as it moves from the ambient state to the supercritical state. Decreasing viscosity of water leads to better mass transfer, enhancing any mass transfer limited chemical reactions (Akiya et al., 2002; Xu et al., 1990; Kuhlmann et al., 1994).
2.4 Products of Hydrothermal Gasification in Sub/Super Critical Water

A huge volume of work can be found on the supercritical water gasification of biomass and models of compounds such as cellulose and glucose, but only a few reports are available on the subject of subcritical water gasification in the literature. This is because, in most studies on hydrothermal gasification, researchers have focused on the gaseous products as supercritical gasification conditions that favour gas formation in higher yields. This work differs from other works in that it focuses on product formation and yield optimization of valuable chemicals in the liquid phase instead of the gases. Also, the current study is the first of its kind to explore the potential of hydrothermal gasification of flax straw in subcritical water.

Looking at literature on this process, Jale et al. (2007) studied the supercritical water gasification of biomass feedstock, including lignocellulosic material and tannery waste, in a batch autoclave at 500°C. In his study, eight different types of biomass feed were used, six of them were agricultural waste and the others were leather wastes (vegetable and chromium tanned). The feedstocks were tobacco stalk (B1), corn stalk (B2), cotton stalk (B3), sunflower stalk (B4), corncob (B5), oreganum stalk (B6), chromium-tanned (B7) waste, and vegetable-tanned waste (B8). The products at the end of the reaction were analysed, and in the gas phase, the major gas products were hydrogen, carbon dioxide, and carbon monoxide. The minor gases were methane, ethane, propane, and propene. He stated that most of the carbon monoxide produced is expected to come from the water soluble organic compounds that were the first products from lignocellulosic material gasification and was finally consumed through water-gas shift.
reaction and methanation. In the liquid phase, a huge number of compounds were reported, which are presented in Table 2.2.

Jale et al. (2007) proposed a plausible reaction mechanism of cellulose decomposition in supercritical water. According to Figure 2.3, adapted from his publication, cellulose is first hydrolysed to sugar units (e.g., glucose and fructose) and further decomposes to acids and alcohols of 1-3 carbons. Portions of the glucose further degrade to furfural, which in turn condenses to phenols and further dehydrate to carboxylic acids. All of these compounds are extremely reactive and readily cracked to gases.
Table 2.2: Content of the aqueous liquid phase (Jale et al., 2007)

<table>
<thead>
<tr>
<th>Material</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>B4</th>
<th>B5</th>
<th>B6</th>
<th>B7</th>
<th>B8</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.21</td>
<td>6.96</td>
<td>7.27</td>
<td>6.82</td>
<td>7.14</td>
<td>7.49</td>
<td>8.52</td>
<td>7.88</td>
</tr>
<tr>
<td>TOC (ppm)</td>
<td>1174</td>
<td>1354</td>
<td>1932</td>
<td>1182</td>
<td>1661</td>
<td>1947</td>
<td>531</td>
<td>589</td>
</tr>
<tr>
<td>Phenol (mg/l)</td>
<td>29.6</td>
<td>540</td>
<td>468</td>
<td>520</td>
<td>49.7</td>
<td>50.6</td>
<td>10.2</td>
<td>46.7</td>
</tr>
<tr>
<td>HMF (mg/l)</td>
<td>3.56</td>
<td>8.01</td>
<td>8.03</td>
<td>3.13</td>
<td>5.56</td>
<td>6.43</td>
<td>&lt; 1</td>
<td>&lt; 1.00</td>
</tr>
<tr>
<td>FU (mg/l)</td>
<td>2.70</td>
<td>3.40</td>
<td>3.12</td>
<td>3.58</td>
<td>2.03</td>
<td>&lt; &lt;1.00</td>
<td>&lt; 1</td>
<td>Nill</td>
</tr>
<tr>
<td>MF (mg/l)</td>
<td>&lt;0.1</td>
<td>&lt; &lt;1.00</td>
<td>1.04</td>
<td>3.58</td>
<td>&lt; &lt;0.10</td>
<td>&lt; &lt;1.00</td>
<td>&lt; 1</td>
<td>&lt;1.00</td>
</tr>
<tr>
<td>Formic acid (mg/l)</td>
<td>54.0</td>
<td>68.6</td>
<td>48.3</td>
<td>82.0</td>
<td>62.4</td>
<td>135.9</td>
<td>22.1</td>
<td>8.1</td>
</tr>
<tr>
<td>Acetic acid (mg/l)</td>
<td>107.0</td>
<td>167.2</td>
<td>324.5</td>
<td>54.8</td>
<td>323.7</td>
<td>393.8</td>
<td>52.9</td>
<td>44.6</td>
</tr>
<tr>
<td>MeOH (%)</td>
<td>0.03</td>
<td>0.02</td>
<td>0.05</td>
<td>0.02</td>
<td>0.04</td>
<td>0.06</td>
<td>Nill</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>Dioxan (mg/l)</td>
<td>4.28</td>
<td>6.76</td>
<td>4.93</td>
<td>17.50</td>
<td>3.20</td>
<td>11.40</td>
<td>8.01</td>
<td>5.91</td>
</tr>
</tbody>
</table>
| HA (mg/l)         | 5.8 | 1.5 | 56.6| 5.1 | 2.2 | 55.0| 5.1 |-
Figure 2.3: Reaction pathway for non-catalytic cellulose decomposition in supercritical water (Kruse et al., 2004)
Sinag et al. (2004) investigated the hydro-pyrolysis of glucose in supercritical water in the presence of K$_2$CO$_3$ as a catalyst. The products observed in the gas phase were basically CO, CO$_2$, CH$_4$, and H$_2$. He reported that the addition of K$_2$CO$_3$ to the glucose solution leads to a significant decrease in CO formation while increasing the yield of H$_2$, CO$_2$, and CH$_4$ per mole of glucose at 500°C. Also, in the liquid phase, the identified products were furfural, methylfurfural, 5-hydromethyl furfural, acetic acid, formic acid, levulinic acid, and acetaldehyde.

Bhaskar et al. (2008) also studied the hydrothermal upgrading of wood biomass at 280°C (subcritical condition), he reported acetic acid, propanoic acid, 2-furancarboxaldehyde, phenol, 2-methylphenol, benzoic acid, methoxyphenol, and butylated hydroxyl toluene as being the products in the aqueous phase. The current research aims at extracting commercially important chemical compounds from the aqueous liquid phase via subcritical water gasification of flax straw.

2.5 USES OF SOME OF THE CHEMICAL COMPOUNDS PRESENT IN THE LIQUID PRODUCT

The production of chemical compounds from biomass is an attractive means of utilization due to their much superior benefits with respect to energy and fuel production, if they are produced for selective purpose. A wide range of chemicals can be produced from biomass in this process. Some of the chemicals and their uses are explain in the proceeding sub-sections.
2.5.1 Formic Acid

Formic acid is a great chemical for different industries. It is mostly used in the textile industry for the dyeing of natural and synthetic fibres, but it is also used for the promotion of fermentation processes in the food industry and as a building block for the production of the sweetener aspartame. It is also employed as a reagent in the production of pharmaceutical and crop-protection agents (Maria et al., 2011).

2.5.2 Acetic Acid

Acetic acid is also an important chemical in industry. The majority of the produced acetic acid is used for the synthesis of polyvinyl acetate, which is use in plastics, coatings, and paints and for cellulose acetate synthesis (Maria et al., 2011). A new application of acetic acid, as reported by Cheung et al. (2002), is for the production of Ca/Mg acetate, an environmental road de-icer.

2.5.3 5-Hydromethyl Furfural (5-HMF)

This chemical is considered a potential future platform compound for several chemical processes, and it is one of the major products of subcritical biomass processing. It is anticipated that it will serve as a precursor for green fuels in the automotive industry. Chheda et al. (2007) reported 5-HMF being used for the production of liquid alkanes. In the chemical industry, it has been revealed that furandicarboxylic acid, an oxidation product of 5-HMF, can be used as a monomer substitute of teraphthalic acid in the process of plastic production.
2.5.4 Other Important Liquid Products

Further important products formed from subcritical water gasification of biomass, as documented in the literature, are:

- Fragmentation products, including glyceraldehydes, dihydroxyacetone, pyruvaldehyde, erythrose, glycoaldehyde, and hydroxyacetone (Antal et al., 1990).
- Dehydration products, including 1, 4-benzentriol and anhydroglucose (Luijkx et al., 1993).
- Condensation products, including soluble and insoluble polymers and carbonized products (Titirici et al., 2007).

The reaction of biomass in hot compressed water is complex and involves several organic compounds. In this research, key compounds, such as phenols, furfural, and organic acids, are identified and quantified. These compounds are formed via different (typical) reaction pathways and are, therefore, a very useful tool to compare complex chemical processes.

A precise study on the effect of process parameters such as temperature, pressure, feed concentration, retention time, acidity, and catalyst on the yield of these compounds will give a better idea of how to optimize the process in favour of the product(s) of interest.

2.6 FURFURAL AS A VITAL CHEMICAL FOR INDUSTRY

Furfural is a key chemical for the production of furan (catalytic decarboxylation) and tetrahydrofuran (through hydrogenation) (Chhedea et al., 2007). Thus, providing a
A biomass-based alternative to petrochemical production of these compounds would be of value (McKillip et al., 1981). Furfural is used primarily in lubricating oil refining and, in condensation with phenol, formaldehyde, acetone, or urea, is used to produce resin with thermosetting properties and extreme physical strength (McKillip et al., 1981). Furfural is solely produced from lignocelluloses biomass by dehydrating pentoses, which are present in considerable amounts in the hemicelluloses of various agricultural residues and hardwoods. This is shown in Figure 2.4, adapted from Runge et al. (2012).

**Figure 2.4:** Dehydration of pentose from hemicelluloses to furfural (Runge et al., 2012)

Furfural obtained from renewable sources has been described in the literature as a key compound that connects the gap between carbohydrate chemistry and petroleum-based industrial chemistry because of its broad range of chemical intermediates and end products that can be produced from this compound for use in the polymer, fuel, and pharmaceutical industries. In this study, one of the objectives is to identify the optimum
process condition for furfural production by hydrothermal gasification of flax straw in subcritical water.

2.7 CATALYSTS FOR FURFURAL PRODUCTION

Few studies have been reported in the literature on the production of furfural in subcritical water. Antal et al. (1988) studied the presence of H$_2$SO$_4$ as a homogeneous catalyst at 523ºK; a higher yield of furfural was observed compared to when there was no catalyst. Antal et al. (1990) also investigated the mechanism of dehydration of fructose in subcritical water at 523ºK; they reported a yield of 47% and 57% for furfural in the absence and presence of H$_2$SO$_4$ as a catalyst. Conventionally, mineral acids such as sulfuric acid are generally used as catalysts to catalyse dehydration of xylose to furfural (Salak et al., 2006). Although in the literature the effect of various solvents and mineral acids on furfural and HMF yield have been studied widely, the effect of a solid acid catalyst on raw biomass subcritical water gasification has not been reported to date. In this research work, a commercially solid acid catalyst will be used, and its effects on the furfural yield will be compared with the yield obtained using a mineral acid catalyst.
3.1 PRECIS

A total of 61 experimental runs were performed to study the hydrothermal gasification of flax straw in subcritical water. This section presents a detailed description of those experimental runs. First, the feed materials, preparation methods, equipments, and gases used are described, followed by description of the catalyst used, feed composition, and operating conditions. A brief description of the experimental setup, reaction process, and products analysis is also included.

3.2 CHEMICALS, GASES, AND EQUIPMENT

3.2.1 Chemicals

- Acetic acid [\text{CH}_3\text{CO}_2\text{H}] (99.99\% purity, Aldrich)
- Formic acid [\text{HCOOH}] (\geq 95 \% purity, Aldrich)
- Phenol [\text{C}_6\text{H}_5\text{OH}] (\approx 99\% purity, Aldrich)
- Furfural [\text{C}_5\text{H}_4\text{O}_2] (99\% purity, Aldrich)
- Ethylene glycol bath fluid (cole-parmer)

3.2.2 Gases

- Nitrogen (UHP, Praxair)
- Helium (UHP, Praxair)
• Argon (Praxair)

3.2.3 Equipments

• 600-mL stainless steel batch reactor (model 5523, Parr Instrument Co.)
• Temperature controller (model 4836, Parr Instrument Co.)
• GC-MS (model 6890/5073, Hewlett- Packard Canada Ltd., Canada)
• Auto injector (model 7683, Hewlett- Packard Canada Ltd., Canada)
• HPLC with RID (model 1100/G1315B, Agilent Technology Canada)
• GC/TCD (Agilent 6890N)
• Flax straw chopper

3.3 FEED MATERIALS AND PREPARATION

Flax straw (*Linum usitatissimum*) was supplied by a farmer in a rural area near of Regina, Saskatchewan, Canada. The straw was sorted out from the accompanying weed/grasses. The selected flax straw was chopped with a flax straw chopper to sizes ranging from 1-3 mm. The chopped flax straw (not dried) was placed in an airtight zipper bag and stored in a desiccator. The drying of the chopped flax straw was not done so as to study the possibility of using the raw feed stock directly from the farm without incurring the drying cost. Ultimate analysis of the flax straw sample was done by Loring Laboratories, Alberta, Canada, to determine the carbon, hydrogen, nitrogen, ash, moisture, and sulphur content. Oxygen was measured by calculating by difference. Samples were analysed using the ASTM (American Society for Testing and Materials)
method. Table 3.1 shows the result of the ultimate analyses on the flax straw sample and literature references.
Table 3.1: Flax Straw Ultimate Analysis Results

<table>
<thead>
<tr>
<th></th>
<th>This study</th>
<th>Tushar (2010) reported</th>
<th>Moilanen(2006) reported</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (wt%)</td>
<td>48.10</td>
<td>45.24</td>
<td>49.1</td>
</tr>
<tr>
<td>Hydrogen (wt%)</td>
<td>5.78</td>
<td>6.25</td>
<td>6.1</td>
</tr>
<tr>
<td>Nitrogen (wt%)</td>
<td>0.68</td>
<td>1.01</td>
<td>1.3</td>
</tr>
<tr>
<td>Ash (wt%)</td>
<td>4.18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sulphur (wt%)</td>
<td>0.07</td>
<td>1.18</td>
<td>0.12</td>
</tr>
<tr>
<td>Oxygen (wt%)</td>
<td>41.91</td>
<td>43.29</td>
<td>40.5</td>
</tr>
</tbody>
</table>
3.4 CATALYST USED

Two different kinds of acid catalyst were used in the study, namely, a mineral acid catalyst and a solid acid catalyst.

3.4.1 Mineral Acid Catalyst

An inorganic acid (HCl) from Aldrich with concentration 1N was used in this study. The different quantities (mL) used and the resulting pH were:

- 1mL of HCl gave pH of 2
- 18mL of HCl gave pH of 1

3.4.2 Solid Acid Catalyst

A commercial H-ZSM-5 catalyst under the trade name “ZEOcat” was purchased from ZEOCHEM AG, Switzerland. H-ZSM-5 is a high performance zeolite catalyst that is highly acidic and contains a high silica to alumina ratio. The characteristic properties of the catalyst are listed in Table 3.2.

<table>
<thead>
<tr>
<th>Product Name</th>
<th>SiO$_2$/Al$_2$O$_3$ [mol/mol]</th>
<th>Crystal size [µm]</th>
<th>Particle size [d$_{50}$]</th>
<th>XRD, cristallinity zeolite [%]</th>
<th>Surface Area [m$^2$/g]</th>
<th>Na$_2$O [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZ-2/25H</td>
<td>20-30</td>
<td>&lt;1</td>
<td>3.0-15.0</td>
<td>&gt;95</td>
<td>400</td>
<td>0.04</td>
</tr>
</tbody>
</table>
The amounts of this catalyst used were 0.5 g and 1.0 g. These amounts were measured using a weight balance for use in the catalytic experiment.

3.5 REACTION FEED STOCK

- Flax Straw: 5 g, 10 g, and 20 g. This amount corresponds to 5 wt%, 10 wt%, and 20 wt%, respectively, of flax straw in the suspension.

3.6 OPERATING CONDITIONS

A series of experiments was performed to determine the influence of process parameters (temperature, pressure, concentration, and retention time) on the yield of liquid and gas product in hydrothermal gasification of flax straw in subcritical water. The retention time represents the time from when a set temperature is reached and at which the reactor was held for a specific time. The experimental runs were divided into three parts:

- Autogenous pressure condition
- Non-autogenous pressure condition
- Catalytic condition.

In the autogenous pressure condition, the rest of the process parameters (temperature, pressure, concentration, and retention time) were varied while the initial reactor pressure was kept at atmospheric conditions (i.e., there was no external supply of pressure to the reactor). In the non-autogenous pressure condition, the initial pressure of the reactor was varied while the other parameters were kept constant. The non-
autogenous pressure condition was actually used to study the effect of pressure on the liquid yield. This was done by selecting the best conditions for liquid product yield in the autogenous pressure condition for use in the non-autogenous runs.

In the catalytic experimental runs, two kinds of acid catalyst were studied to determine their effects on the yield of a particular product of interest. The pH of the suspension and amount of solid acid catalyst was adjusted with the mineral acid catalyst and also the weight of the solid acid catalyst, respectively. The aim was to study how pH and catalyst amounts affect the yield of our product of interest. A comprehensive range and values of each of the parameters used is shown below:

- Temperature : 175, 200, 225, 250, 275, and 325°C
- Pressure (initial reactor gauge pressure) : 0, 20, 40, 60, and 80 bar
- Retention time: 0, 60, 90, 120 min
- Concentration: 5, 10, 20 wt%
- pH: 1,2
- Catalyst amount : 0.5, 1 g

3.7 EXPERIMENTAL SETUP AND PROCEDURE

3.7.1 Schematic and Description of Experimental Setup

As shown in Figure 3.1, the reaction was carried out using a using a 600 mL stainless steel batch reactor (model 5523, Parr Instrument Co., Moline, IL). The removable reactor head assembly consisted of a magnetic drive connected to a stainless steel (T316) stirring shaft and two adjustable four-rectangular-blade impellers (diameter of about 1.5 inch.) of which one was positioned almost at the bottom of the vessel and the other was about 2.5 inches above the bottom one.
Figure 3.1: Schematic diagram of experimental setup used for the process
The positions of these impellers were held constant throughout the experiments. In addition, the reactor also had a 0-3000 psi Bourdon-type pressure gauge; gas inlet, gas release, and liquid sampling valves; a preset safety rupture disk; a J-type thermocouple; a dip tube for gas introduction and sample removal; and a cooling coil for maintaining the process at a constant temperature irrespective of the temperature rise caused by overshooting. The cooling system was regulated by a solenoid valve. The heat was supplied to the reactor by a furnace in which the reactor vessel was inserted and regulated by a temperature controller (model 4836, Parr Instrument Co., Moline, IL), whereas the temperature of the reaction mixture was measured by a J-type thermocouple. The temperature accuracy of the controller was within (±0.1%). The UHP nitrogen gas was supplied by Praxair.

3.7.2 Typical Experimental Run

In a typical experimental run, a known amount of flax straw (5, 10 and 20 g) was weighed and placed in the reactor and a known volume of distilled water was added to achieve the desired weight percent (5, 10, 20 wt%) of flax straw in water in the autoclave. The reason for using distilled water is because of its low salinity. After loading the suspension, the autoclave was purged with nitrogen gas for 10 min to remove the air in the reactor. The reactor was then heated to a specific set temperature (175, 200, 225, 250, 275, and 325°C) and was held at this temperature for a given time (0, 60, 90, and 120 min); this time is referred to as the retention time. At the end of the reaction, the reactor was cooled to room temperature under atmospheric conditions to allow for the
condensation of the gases formed. After cooling, the amount of gas formed was measured, and the gas composition was analysed online with an online gas chromatograph equipped with a thermal conductivity detector (GC-TCD). The aqueous solution was filtered from the char and analysed with a GC-MS /HPLC-RID. The char samples were also analysed for CHNS (carbon, hydrogen, nitrogen, and sulphur) content.

In the case of a non-autogenous experimental runs, the initial pressure of the reactor was increased to a set pressure (20, 40, 60, and 80 bar) with nitrogen gas before the reaction commenced.

Also, for the catalytic experimental runs, the pH of the suspension was adjusted by adding a certain quantity of inorganic acid (HCl) to it. Then, 1 mL of 1N HCl was added to get a pH of 2, while 18 mL of 1N HCl was added to the suspension to achieve a pH of 1. In the case of solid acid catalyst (H-ZSM-5), the required quantity (0.5 and 1 g) was weighed and added to the flax straw-water suspension before starting the runs.

3.8 PRODUCTS ANALYSIS

3.8.1 Gaseous Products Analysis:

A gas chromatograph (Agilent Technologies 6890) equipped with two columns (Hayesep Q and molecular sieve) and a thermal conductivity detector (TCD) was used for analysing the gases. For calibration of the GC, standard gas mixtures were used. Helium was used as the carrier gas.
3.8.2 Liquid Products Analysis:

The amounts of organic acids, furfural, and phenol were measured with a gas chromatograph coupled with a mass selective detector (GC-MS). A GC alone can separate compounds in a mixture with a good resolution, but it cannot identify them. A MS cannot separate them but can provide detailed structural information for most compounds. A combination of these two techniques provides both quantitative and qualitative information within a single run. The GC-MS instrument (model 6890/5073) was obtained from Hewlett-Packard Canada, Ltd., Montreal, Quebec, Canada. Chromatographic capillary columns of different stationary phases and polarities were tested to see which one gives a better separation of the liquid products. These columns were HP-Innowax (high-polarity) and HP-35MS (intermediate-polarity) having cross-linked poly(ethylene glycol) and 35% phenylmethylsiloxane, respectively, as stationary phases. Both columns had the same dimensions of 0.25 μm thickness x 0.25 mm i.d x 30 cm length and were obtained from Hewlett-Packard Canada, Ltd., Montreal, Quebec, Canada. After several tests, the HP-35 column was found to give a better separation of the liquid product from water.

The introduction of sample was done using an auto sampler/auto injector (model 7683, Hewlett-Packard Canada, Ltd., Montreal, Quebec, Canada). The auto injector volume was reproducible to within 0.3% relative standard deviations (RSD) in terms of percentage area of the peaks. Identical GC-MS operating conditions were applied to all columns. For a typical run, a 1 μL sample was injected at the GC inlet set at 250°C using a split injection mode with a split ratio of 5:1. The GC oven was initially set at 37°C and ramped to 210°C at a rate of 10 C/min. The temperature was kept at 210°C for as long as
20 min to ensure complete elution of all degradation products of flax straw. Ultra-high-purity (UHP)-grade helium was used as the carrier gas and was regulated at a constant flow rate of 1 mL/min. The GC-MS interface, MS quadrupole, MS source, and EM voltage were kept at 250°C, 150°C, and 230°C, and 1858 V, respectively. MS scan mode was used with a mass range from 10 to 300. The products were identified by matching the mass spectra of the chromatographic peaks with commercial mass spectra of the National Institute of Standards and Technology (NIST) database (1998 version). A matching technique that compared the mass spectra of the GC-separated components with the NIST database was used for the initial product identification. Verification of some of the species was subsequently performed by comparing both the mass spectra and the GC retention time of commercially available pure standards with those of the initially identified components. The mass spectral pattern of the sample was found to be in excellent conformity with those of the NIST database and the pure standard.

The HPLC-RID was used to confirm the separation results gotten from the GC-MS for formic acid and acetic acid, since the chromatogram peaks of both acids were so close when using GC-MS. This instrument was equipped with a refractive index detector (RID) and an on-line degasser (model 1100/G1315B/G1322A, Agilent Technologies Canada, Mississauga, Ontario, Canada). A Zorbax SB-Aq column of 4.6-mm i.d. x 150-mm length was selected based on Agilent Technology recommendations. The flow rate was 1.0 mL/min, temperature was 35°C, and a UV detector of 210 nm was used. The mobile phase was 0.05 kmol/m³ potassium dihydrogen phosphate solution (KH2PO4) adjusted to a pH of 2.6 by adding 85% w/w phosphoric acid (H3PO4). For a typical analysis, as much as 8 μL of sample was injected to ensure visualization of low-
concentration products. The columns were kept at 30°C. All analyses were done using a simple isocratic approach in which 100% of a single mobile phase flowing at a rate of 1 mL/min was used throughout the analysis (Supap et al., 2006). The RID optical unit was set at a temperature of 30°C and operated under positive mode. Prior to the analysis, samples were diluted to 1:40 with nano-pure water, followed by filtration using a 0.20 μm nylon membrane filter. All mobile phases were degassed in an ultrasonic bath for at least 3 h and filtered through a 0.20 μm nylon membrane filter prior to use.

3.9 EQUATIONS USED TO CALCULATE YIELD AND CONVERSION

The equation representing flax straw gasification is subcritical water is given by:

\[ \text{CH}_{1.5}\text{O}_{0.62} \xrightarrow{\text{water}} \text{CO} + \text{CO}_2 + \text{CH}_4 + \text{char} + \text{Liquid Products} + \text{tar(\text{CH}_n\text{O}_x)} + \text{H}_2\text{O} \] (3.1)

The chemical formula of flax straw from the above equation was obtained from Tushar’s work (Tushar, 2010) on Pyrolysis of flax straw.

This equation was used to develop the kinetic model for flax straw degradation in subcritical water.

The definition of selectivity used in this calculation is shown below:

Yield of “A” = \frac{\text{moles of } A}{\text{gram of flax straw used}} \left( \frac{\text{mols}}{\text{g}} \right)

where “A” is the liquid or the gas product.
A detailed calculation of the products yield is shown in Appendix A.

Conversion of Flax Straw ($X_A$): Flax straw conversion was calculated from CHNSO (ultimate analysis) analysis of the char remaining at the end of the reaction. The conversion was in terms of the amount of carbon remaining with respect to the amount initially present in the flax straw.

\[
\text{Carbon Conversion (Xc)} = X_A = \frac{W_{C_i} - W_C}{W_{C_i}}
\]

where \( W_{C_i} \) = initial weight of carbon in the flax straw before the reaction.

\( W_C \) = weight of carbon in the char at the end of the reaction.
CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 LIQUID PRODUCT COLOUR TRANSFORMATION

The colour of the liquid products collected after filtration at the end of each experiment, which were carried out at different temperatures in the range of 200 to 325°C (with 25°C temperature intervals) under autogenous pressure (and external pressure) were found to change with temperature, as noted in Figure 4.1. From the figure, it is clear that the liquid product colour transitions from being dark yellow to light yellow, which signifies a significant decrease in the total organic component in the liquid yield as a function of temperature. The above observation is quite obvious, as the temperature is known to accelerate the gasification efficiency of the process, thereby transforming the liquid to gaseous products.
Figure 4.1: Appearance of liquid phase at the end of the reaction at various temperatures.
4.2 QUALITATIVE AND QUANTITATIVE ANALYSIS OF THE LIQUID PRODUCTS.

The liquid product obtained from the hydrothermal gasification process contains a wide variety of organic compounds. According to the initially proposed mechanism as discussed in Chapter Two (Figure 2.3) of this thesis, cellulose, which is a major component of flax straw, hydrolyses to sugar units (e.g., glucose and fructose) in subcritical water; it is further decomposed to acids and alcohols. Part of the glucose is degraded to furfural, which is further condensed to phenols and dehydrated to acids. All of these compounds are highly reactive and are readily cracked to gases. In the current study, three different temperatures in the subcritical region were chosen to investigate the effect of temperature on the liquid product distribution in the hydrothermal gasification of flax straw. The temperatures were 225, 275 and 325ºC. A chromatogram of the liquid product showing the peaks of the compounds present is shown in Figure 4.2.

As seen from the chromatogram, the liquid product samples contain a wide variety of different organic compounds. Table 4.1 lists the various organic compounds detected in the liquid phase. As a huge library of organic compounds was detected, it is beyond the scope of the current work to quantify all of them. Therefore, a selected few commercially and fundamentally important components were chosen and quantified. These included furfural, phenol, acetic acids, and carboxylic acids. In order to estimate the concentrations of these compounds, a calibration curve was generated using known concentrations of these compounds to produce a chromatogram (such as given in Figure 4.2), as explained in Section 3.8.2. The area of each peak was then used in calculating the concentration of the compounds of unknown samples from the calibration curve shown in
Appendix A. The effect of process parameters on the yield of these four compounds was studied, and the corresponding results are presented in section 4.4.
Figure 4.2: GC-MS chromatogram of the liquid product formed at (a) 225°C  
(b) 275°C  (c) 325°C
Table 4.1: GC-MS Results of detected compounds in the liquid phase

<table>
<thead>
<tr>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>2- Propanone</td>
</tr>
<tr>
<td>2- Butanone</td>
</tr>
<tr>
<td>5-Hydro Methyl Furfural</td>
</tr>
<tr>
<td>Acetaldehyde</td>
</tr>
<tr>
<td>Acetone</td>
</tr>
<tr>
<td>Acetic acid</td>
</tr>
<tr>
<td>Butanioc acid</td>
</tr>
<tr>
<td>Ethanol</td>
</tr>
<tr>
<td>Formic acid</td>
</tr>
<tr>
<td>Furfural</td>
</tr>
<tr>
<td>Furan</td>
</tr>
<tr>
<td>Methyl Alcohol</td>
</tr>
<tr>
<td>Phenol</td>
</tr>
<tr>
<td>Propanoic acid</td>
</tr>
</tbody>
</table>
4.3 QUALITATIVE AND QUANTITATIVE ANALYSIS OF THE GASEOUS PRODUCTS

The influence of temperature on the gaseous product distribution was investigated with the help of a GC/TCD. The resultant analyses revealed the existence of permanent gases including CO$_2$, CO, and traces of CH$_4$ in the gaseous product stream, with CO$_2$ being most abundant. The non-detection (non-formation) of H$_2$ can be explained by one of the following two possibilities: either incomplete gasification or H$_2$ consumption occurred during the course of the reaction as H$_2$ is a very reactive gas. The evidence for the later possibility comes from previous studies, which have shown that H$_2$ formed via the water gas shift reaction can react further with organic compounds to form hydrogenated products (Minowa et al., 1999). Parametric sensitivity studies on the effect of various process variables on the gas product distribution were also studied and are reported in a later part of this chapter.
4.4 EFFECT OF PROCESS PARAMETERS ON THE LIQUID PRODUCT YIELD

A number of experiments were conducted to study the effect of various process parameters on the yield of furfural, phenol, acetic acid and formic acid. The results are presented in the following sub-sections.

4.4.1 Effect of temperature

In order to study the effect of temperature on the liquid product yield, three different temperatures were chosen, which are 225, 275 and 325ºC. In a typical experiment, a fixed and known amount of flax straw was used at each temperature under autogenous pressure conditions, and the reaction retention time was set at 0 min. The results of the above devised experiments are shown in Figures 4.3 and 4.4.

In Figure 4.3, a 5 wt% of flax straw was used for the reaction. At 225ºC, the compounds formed were acetic acid, formic acid, and phenol, with the highest yield being acetic acid. As the temperature was increased to 275ºC, formic acid was not detected due to increase in gasification efficiency, and the other products observed were acetic acid, furfural, and phenol. When the temperature was further increased to 325ºC, furfural formation diminished while phenol formation increased. Acetic acid still remained the pre-dominant product with a yield of 0.0009 mol/g of flax straw.

From Figure 4.3, it can be seen that the temperature plays a vital role in the degradation and hydrolyses of flax straw in subcritical water. Increasing the temperature increases the flax straw conversion (or gasification efficiency), which, in turn, promotes the free radical reactions and results in the formation of fewer specified products. From
Figure 4.3, it is observed that increasing the temperature from 225 to 325ºC decreases the yield of furfural and formic acid while favouring the formation of phenol. This can be attributed to the existence of the multiple reaction pathways present in the process. Hence, it can be inferred that higher temperatures promote phenol formation while furfural formation is favoured at lower temperatures with the optimum being 275ºC.

Similar trends were noted, as shown in Figure 4.4, when 10 wt% of flax straw was subjected to the above stated conditions, although the overall yield in mol/g flax straw was low due to incomplete gasification of a larger amount of flax straw. On the whole, the liquid product yield decreased with increasing temperature due to increase in the gasification efficiency, which converts low molecular liquids such as formic acid to permanent gases. The above observations correlates well with the liquid product colour variations noted in an earlier section.
**Figure 4.3:** Effect of the reaction temperature on the liquid product yield at 0 min retention time, initial reactor gauge pressure of 0 bar, and 5 wt% of flax straw
Figure 4.4: Effect of reaction temperature on the liquid product yield at 0 min retention time, initial reactor gauge pressure of 0 bar, and 10 wt% of flax straw.
4.4.2 Effect of retention time

The effect of retention time on the liquid product yield was studied at three different temperatures. In each case, the amount of flax straw and the initial reactor pressure was kept constant while the retention time was varied from 0 to 120 min. This retention time represents the time for which the reaction is carried out, after attaining the set temperature, followed by immediate cooling. The corresponding results are shown in Figures 4.5, 4.6, and 4.7 respectively. In the experiments carried out at 225ºC with varying retention times (Figure 4.5), the results reveal that increasing the retention time decreases the overall yield of formic acid and furfural while increasing the overall yield of acetic acid. A similar trend is seen when 10 wt% flax straw was subjected to the same conditions. The most plausible explanation for the above noted trends could be that increasing the retention time improves the overall gasification efficiency, thereby gasifying the reactive components and allowing the system to form more stable components such as acetic acid.

In Figure 4.6, where the retention time effect was studied at 275ºC, it was seen that the increase in retention time leads to a drastic decrease in the yield of furfural and formic acid while the yield of phenol increases. This is a result of the increase in gasification efficiency associated with the high temperature, which pushes the liquid products to the gas phase with increasing retention time. The effect of retention time on the yield of acetic acid under these conditions was almost negligible. The same trend was also seen when a 10 wt% flax straw was also subjected to the same condition.
In Figure 4.7, which provides results on the effect of retention time at 325°C, it was observed that the yield of acetic acid decreases as the retention time increases suggesting decarboxylation reaction of the acids to gases was occurring. Phenol yield increased rapidly with increase in retention time. This might be because at a higher temperature and longer retention time, condensation of aldehydes leads to the formation of a large number of cyclic aliphatic ketones, aromatic hydrocarbons, and aromatic aldehydes (Sinag et al., 2003). Acetic acid yield was the highest at all retention times across the three temperatures.
Figure 4.5: Effect of retention time on the liquid product yield at 225°C, initial reactor gauge pressure of 0 bar, and (a) 5 wt% flax straw, (b) 10 wt% flax straw
Figure 4.6: Effect of retention time on the liquid product yield at 275°C, initial reactor gauge pressure of 0 bar, and (a) 5 wt% flax straw, (b) 10 wt% flax straw
Figure 4.7: Effect of retention time on the liquid product yield at 325°C, initial reactor gauge pressure of 0 bar, and (a) 5 wt% flax straw, (b) 10 wt% flax straw
4.4.3 Effect of feed concentration

The effect of feed concentration on the liquid product yield was studied by varying the amount of flax straw used from 5 wt% to 20 wt%, and the corresponding results are shown in Figure 4.8. Here, the temperature, initial reactor pressure, and retention time were all kept constant. The results revealed that as the feed concentration increases, the yield of the compounds (acetic acid, formic acid, furfural, and phenol) decrease. This can be attributed to the low gasification efficiency observed. A high amount of feedstock is more difficult to gasify leading to lower yields of the products. However, to achieve a thermal efficiency high enough to establish an economic process, the gasification of a high concentration feedstock is necessary. According to Antal et al. (2000), it is believed that high temperature, high heating rate, and catalyst are required in the gasification of large amounts of feedstock.
Figure 4.8: Effect of feed concentration on the liquid product yield at 225°C, 0 retention time, and initial reactor gauge pressure of 0 bar
4.4.4 Effect of pressure

The influence of pressure on the liquid product yield was studied by varying the initial pressure of the reactor from 0 to 80 bars. In each case, the initial pressure of the reactor was increased using an inert gas (nitrogen gas) cylinder at a set pressure before the reaction commenced, while keeping the rest of the parameters constant. The results, as shown in Figure 4.9, reveal that as the pressure is increased, the yield of acetic acid, formic acid, furfural, and phenol increases to a greater extent. The results show that pressure is an important parameter in subcritical water gasification of flax straw. The reason for this increase can be attributed to the role of water in chemical reactions in subcritical water. Firstly, the properties of water such as density, static dielectric constant, and ion product increase with pressure. As a result of this, the ionic reaction rate, which is necessary for liquid product formation, increases while the free-radical reaction, which is necessary for gas formation, decreases with increasing pressure. Secondly, the hydrolysis reaction rate, which is influenced by the ion concentration (H\(^+\) and OH\(^{-}\)), plays an important part in the flax straw gasification under these conditions. With increasing pressure, the ion product increases resulting in an increase in the hydrolysis rate.
Figure 4.9: Effect of pressure on the liquid product yield at 225°C, 0 retention time, and 5 wt%
4.5 EFFECT OF PROCESS PARAMETERS ON THE GASEOUS PRODUCT YIELD

The effect of temperature and retention time on the yield of the gas product was also investigated as well. The result of our finding is presented in the sub-sections below.

4.5.1 Effect of temperature

A separate set of experiments was carried out in a similar fashion as carried out above to study the qualitative and quantitative analysis of the gaseous product streams. In each case, the amount of flax straw used and the initial reactor pressure was kept constant while the reaction retention time was set at zero. The results of this study are shown in Figure 4.10. Four main gases were identified. Methane gas was produced at a temperature of 275ºC and an almost negligible amount of ethane gas was seen at a temperature of 325ºC and above. Meanwhile, CO and CO$_2$ were seen at all the temperatures investigated. As observed in Figure 4.10, temperature has a significant effect on the yield of the gases. As temperature is increased, the gas yield increases due to the promotion of free radical reactions. The yield of CO$_2$ was the highest, followed by CO. Formation of H$_2$ gas was not observed. The likely reasons could be incomplete gasification and/or H$_2$ consumption in the process.
Figure 4.10: Effect of reaction temperature on the gas yield at 0 min retention time, initial reactor gauge pressure of 0 bar, and 10 wt% of flax straw
4.5.2 Effect of retention time

The effect of retention time on the gas product yield was studied at three temperature points (225, 275, and 325 ºC). In each case, a 10 wt % of flax straw was used and the initial pressure of the reactor was set at atmospheric pressure. The retention time was varied between 0 to 120 min. The results of this investigation are shown in Figures 4.11, 4.12, and 4.13, respectively. The results in Figure 4.11, in which the effect of retention time was studied at 225ºC, reveal that increasing the retention time from 0 to 120 min actually increases the yield of the gases with CO₂ gas giving the highest yield. The same trend was observed at 275ºC in Figure 4.12, but the increase was not as great as in the case of 225ºC. At 325ºC, the yield of the gas reached its maximum with increasing retention time, but the difference was not significant when compared to the gas yield observed at 275ºC, as shown in Figure 4.13. In summary, we can say that retention time has a more significant effect on the gas yield at a lower temperature than at a higher temperature.
Figure 4.11: Effect of retention time on the liquid product yield at 225°C, initial reactor gauge pressure of 0 bar, and 10 wt% flax straw
**Figure 4.12:** Effect of retention time on the liquid product yield at 275ºC, initial reactor gauge pressure of 0 bar, and 10 wt% flax straw.
Figure 4.13: Effect of retention time on the liquid product yield at 325°C, initial reactor gauge pressure of 0 bar, and 10 wt% flax straw
4.6 OPTIMIZING THE YEILD OF FURFURAL

One of the goals of this research was to optimize the process to increase the yield of the desired product (furfural). From our parametric study, it was seen that increasing temperature and retention time does not favour the yield of furfural, but a lower temperature and an increase in the initial pressure of the reactor does. In this study, two approaches were used to optimize the furfural yield. In the first approach, the temperature of the process was reduced to find the optimum temperature for furfural. In the second approach, two kinds of catalyst were tested to determine their catalytic effects on the yield of furfural. Our findings are presented in sections 4.61 and 4.62 of this thesis.

4.6.1 Determination of Optimum Temperature for Furfural Yield

To determine the optimum temperature for furfural yield, another series of experiments was performed at lower temperatures, from 100°C to 275°C, with a 5 wt% of flax straw. The initial pressure of the reactor was kept at atmospheric and a 0 min retention time was used. The reason this temperature range was selected is that, according to our parametric study, at temperatures above 275°C, the yield of furfural was tending to zero, indicating that a higher temperature does not favour furfural yield. The results of our findings are shown in Figure 4.14, which reveals that the optimum temperature for furfural yield is 250°C. Below this temperature, furfural formation is not complete, and above this temperature, the yield starts decreasing. This optimum temperature was used with the second approach tested for optimizing the yield of furfural.
Figure 4.14: Determination of optimum temperature for furfural yield using 5 wt% of flax straw, 0 min retention time, and initial reactor gauge pressure of 0 bar
4.6.2 Acid Catalysed Reaction

Furfural is produce by the hydration of pentosan to pentose, which is then dehydrated to furfural (Runge et al. (2012). This reaction is acid catalysed. Equations 4.1 and 4.2 show the reaction.

\[(C_5H_8O_4)_n + nH_2O \rightarrow nC_5H_{10}O_5 \quad (4.1)\]

\[C_5H_{10}O_5 - 3 x H_2O \rightarrow C_5H_4O_2 \quad (4.2)\]

The mechanism of acid- catalysed dehydration of pentose to furfural takes place in three steps:

- Addition of a proton to the molecule to be converted
- Rearrangement of the molecules activated (destabilized) by the added proton
- Withdrawal of the added proton to yield a neutral product molecule.

In this case, the molecule to be converted is the pentose and the neutral product form is the furfural. The mechanism of this process is shown in Figure 4.15.
In this study, two kinds of acids were tested to observe their contribution to the yield of furfural. These catalysts were:

- HCl acid (homogeneous mineral acid catalyst)
- H-ZSM-5 (heterogeneous solid acid catalyst)

These catalysts act as proton-donors in the reaction, and their catalytic effects on the yield of furfural are presented in sections 4.6.2.1 and 4.6.2.2.
Figure 4.15: Mechanism of pentose dehydration to furfural (Elsevier)
4.6.2.1 EFFECT OF ACIDITY (pH) ON FURFURAL YIELD

Figure 4.16 shows the effect of pH on the yield of furfural using 1N HCl as the homogeneous mineral acid catalyst. In this study, a 5 wt% of flax straw sample was gasified at 250°C (optimum temperature for furfural yield) with an initial reactor pressure of 40 bar and a retention of 0 min. The pH of the reaction mixture was maintained at pH 2 and 1 by the addition of 1 mL and 18 mL of 1N HCl, respectively. The results of the acid catalyzed reactions were compared with those from a non-catalyzed reaction in order to be able to draw useful conclusions.

As shown in Figure 4.16, the yield of furfural in the non-catalysed reaction did not exceed 0.0001 mol/ g of flax straw. Decreasing the pH of the suspension to 2.0 increased furfural yield to 0.0005 mol/g of flax straw, and greater yield is observed when the pH of the suspension is decreased to 1.0. This result reveals that acidity plays an important role in the rapid decomposition of the hemicelluloses present in flax straw to pentosan, which is hydrated to pentose and finally dehydrated to furfural. It is also observed that, under acidic conditions (pH ≤ 2), the yield of acetic and formic acid decreases. This might be as a result of a shift in the reaction pathway from acetic and formic acid formation to furfural formation.
Figure 4.16: Effect of acidity of furfural yield at 250°C, initial reactor gauge pressure of 40 bar, and 5 wt% flax straw
4.6.2.2 EFFECT OF SOLID ACID CATALYST (H-ZSM-5) ON FURFURAL YIELD

In this study, a certain amount of H-ZSM-5 catalyst was added to the reaction mixture containing 5 wt% of flax straw under operating conditions of 250°C (optimum temperature for furfural yield), atmospheric pressure, and 0 min retention time. H-ZSM-5 is a highly acidic catalyst. The effect of the catalyst was investigated by varying the amount of H-ZSM-5 used from 0.5 to 1 g, and the results obtained were compared with a non-catalyzed reaction under similar operating conditions. As shown in Figure 4.17, H-ZSM-5 acid catalyst shows excellent catalytic activity for furfural yield. Increasing the amount of the solid catalyst from 0.5 g to 1 g increases the yield of furfural from 0.0006 mol/g of flax straw to 0.0008 mol/g of flax straw. This is probably due to the large number of catalytically active acid sites and the high surface area of the H-ZSM-5 catalyst. The yield of formic and acetic acid was also seen to decrease, just as in the case of the HCl catalyzed reactions. Other secondary reactions such as the formation of 5-hydromethyl furfural (HMF) were also found to be favoured in the process.
**Figure 4.17:** Effect of H-ZSM-5 on furfural yield at 250°C, initial reactor gauge pressure of 0 bar, and 5 wt% flax straw
4.6.2.3 COMPARING THE ACTIVITY OF BOTH CATALYSTS

Looking at the activity of both catalysts towards the yield of furfural, it can be seen that both catalysts selectively increase the yield of furfural compared to other compounds in the aqueous phase product. The effect of acid catalyst on the reaction pathway is represented in the flow diagram shown in Figure 4.18. However, when HCl was used, some side reactions were seen to be taking place in the liquid phase that led to the formation of undesirable products such as pentatonic acid. In terms of additional separation costs associated with using a catalyst, H-ZSM-5 provides a better alternative since it can be separated from the liquid products by filtration, thereby saving costs.
Figure 4.18: Acid catalysed reaction pathway for flax straw gasification in sub critical water
4.7 EFFECT OF H-ZSM-5 CATALYST ON THE GAS YIELD

The effect of the solid acid catalyst (H-ZSM-5) on the gas product yield was also investigated, and the results obtained were compared with the non-catalysed reaction under similar operating conditions. In this study, a 1g of H- ZSM-% catalyst was added to the reaction mixture containing 10 wt% of flax straw under the operating conditions of 325ºC (optimum temperature in this process for gas yield) and 0 min retention time. As shown in Figure 4.19, H-ZSM-5 acid catalyst shows excellent catalytic activity for the yield of H\textsubscript{2} and CO\textsubscript{2}. H\textsubscript{2} gas, which was not present in the non-catalytic experiments, was seen in this condition. CO, CH\textsubscript{4}, and C\textsubscript{2}H\textsubscript{6} yield decreased when compared with the non-catalysed reaction. This can be attributed to the fact that three major competing reactions are occurring during the gasification of biomass in water (Chowdhury et al., 2010) as shown below:

- Steam reforming :
  \[ \text{CH}_x\text{O}_y + (1 - y)\text{H}_2\text{O} \rightarrow \text{CO} + \left(2 - y + \left(\frac{x}{2}\right)\right)\text{H}_2 \]  (4.3)

- Water gas shift reaction:
  \[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]  (4.4)

- Methanation reaction
  \[ \text{CO} + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \]  (4.5)
  \[ \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \]  (4.6)

The water gas shift and steam reforming reaction pathway was selectively favoured in this case.
Figure 4.19: Effect of H-ZSM-5 on the gas yield at 325°C, initial reactor gauge pressure of 0 bar, 10 wt% flax straw, and 0 min retention time
4.8 KINETIC STUDIES

4.8.1 Empirical Rate Model

The kinetics of flax straw degradation in subcritical water were studied at three different temperatures (225, 275 and 325ºC) with a 10 wt% flax straw and initial reactor gauge pressure of 0 bar. The retention time was varied from 0 to 120 min. The overall equation of the reaction used for the development of the kinetic rate model for flax straw decomposition in subcritical water is given below:

\[
\text{CH}_{1.5}\text{O}_{0.62} \xrightarrow{\text{water}} \text{CO} + \text{CO}_2 + \text{CH}_4 + \text{char} + \text{Liquid Products} + \text{tar(C}_{n}\text{O}_x) + \text{H}_2\text{O}
\]

(3.1)

The rate of degradation or conversion \( \left( \frac{dX_A}{dt} \right) \) is a function of a temperature-dependent rate constant (k), reaction order (n) and a temperature-independent function of conversion \( (1-X_A) \).

For a batch reactor process (Levenspiel, 1999),

\[
-r_A = \frac{dX_A}{dt} = k(1 - X_A)^n
\]

(4.7)

The rate constant (k) is described by the Arrhenius expression as:

\[
k = A e^{\frac{E_a}{RT}}
\]

(4.8)

Where  

\( A = \) pre exponential factor or collision factor 

\( E_a = \) activation energy, J/mol 

\( T = \) reaction temperature, K 

\( R = \) molar gas constant, 8.314 J/mol/K
The flax straw conversion ($X_A$) was calculated from the CHNSO analysis (ultimate analysis) of the char collected at the end of each experiment and was defined in terms of carbon conversion:

$$X_A = X_C = \frac{W_{C0} - W_C}{W_{C0}}$$  \hspace{1cm} (4.9)

where $X_C$ = Carbon conversion

$W_{C0}$ = initial weight of carbon in the flax straw

$W_C$ = weight of carbon present in the resultant char

Substituting Equation 4.8 into 4.7 gives:

$$\frac{dX_A}{dt} = Ae^{\frac{-E}{RT}}(1 - X_A)^n$$  \hspace{1cm} (4.10)

Taking the natural log of Equation 4.4 gives

$$\ln \left( \frac{dX_A}{dt} \right) = \ln A - \frac{E}{RT} + n \ln (1-X_A)$$  \hspace{1cm} (4.11)

The values of $A$, $E$, and $n$ in Equation 4.10 were determined through a multi-linear regression of the data for each stage using NLREG software (details are given in Appendix C).
4.8.2 Experimental Rate of Reaction

The rate of carbon degradation in flax straw was determined by plotting a graph of carbon conversion against retention time. As shown in Equation 4.7, the slope of the graph at any point gives the rate:

$$-r_A = \frac{dX_A}{dt} \quad (4.7)$$

Details on this method of analysis can be found in Levenspiel (1999) as discussed in Chapter 3 above. The \(X_A\) vs. retention time (RT) graphs were drawn for all three temperatures and are shown in Figure 4.20. The highest conversion was 40% at 325ºC. The experimental rates of the reactions were obtained from Figure 4.20 as the derivatives of the conversion (\(X_A\)) vs. reaction time (t), and the results are presented in Table 4.2.

An important point to be noted here is that the curves have been generated using data analysis and a graphing tool called “Origin Pro. 8”. Details about the curve fitting and equations are given in Appendix B.

The reaction time (t) in this case is defined as:

Time taken to reach a set temperature + retention time (RT)
Figure 4.20: Carbon conversion for at different retention times for temperatures of 225, 275, and 325ºC
Table 4.2: Experimental kinetics data table

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>dXA/dt [mol/(g* min)]</th>
<th>Xc</th>
</tr>
</thead>
<tbody>
<tr>
<td>498</td>
<td>0.000766</td>
<td>0.139</td>
</tr>
<tr>
<td>498</td>
<td>0.000729</td>
<td>0.154</td>
</tr>
<tr>
<td>498</td>
<td>0.000693</td>
<td>0.176</td>
</tr>
<tr>
<td>548</td>
<td>0.000937</td>
<td>0.325</td>
</tr>
<tr>
<td>548</td>
<td>0.00092</td>
<td>0.34</td>
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<td>548</td>
<td>0.000906</td>
<td>0.361</td>
</tr>
<tr>
<td>498</td>
<td>0.000789</td>
<td>0.124</td>
</tr>
<tr>
<td>548</td>
<td>0.000853</td>
<td>0.38</td>
</tr>
<tr>
<td>548</td>
<td>0.000854</td>
<td>0.355</td>
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<td>598</td>
<td>0.00139</td>
<td>0.39522</td>
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<td>598</td>
<td>0.00132</td>
<td>0.3941</td>
</tr>
<tr>
<td>598</td>
<td>0.00131</td>
<td>0.4051</td>
</tr>
</tbody>
</table>
4.8.3 Estimation of Parameters of the Rate Model

Estimation of parameters for the rate model in Equation 4.10 was based on the minimization of the sum of the residual squares of the reaction rates by the Gauss-Newton and Levenberg-Marquardt algorithm using non-linear regression software (NLREG). The values obtained for the parameters are presented in Table 4.3. The NLREG code is given in Appendix C. The validation of the models was based on the determination of percent average absolute deviation (AAD%) between the predicted rate using the proposed kinetic model and the experimentally obtained rate. An AAD of 8.4% was achieved for the model.

The formula for calculating AAD% is

\[
AAD\% = \frac{|\text{Experimental rate} - \text{Predicted rate}|}{\text{Experimental rate}} \times 100\%; \quad (4.12)
\]

Besides calculating AAD%, a parity plot of the experimental rate vs. predicted rate was also drawn to depict how well the models fit the experimental data; this is shown in Figure 4.21. From the parity plot, it can be concluded that the experimental rate and model predicted rate match perfectly. Therefore, the empirical rate model of Equation 4.10 can be written as:

\[
-r_A = \frac{dX_A}{dt} = 8.3156 \times 10^{-1} e^{-27969.63/RT} (1 - X_A)^2 \quad (4.13)
\]
### Table 4.3: Estimated parameters of the rate model

<table>
<thead>
<tr>
<th>Estimated Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong></td>
</tr>
<tr>
<td>8.3156 x 10^-1</td>
</tr>
</tbody>
</table>
Figure 4.21: Parity plot of experimental vs. predicted rate
CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusions can be drawn from this research work:

- Increasing the process temperature results in an increase in the gasification efficiency and gas yield.
- Lower temperatures (≤ 250°C) favour the formation of liquid products in abundance.
- For gasification of a higher concentration (amount) of feed stock (flax straw), a higher temperature and a catalyst are essential.
- Retention time has a greater effect on the gas product yield than the liquid product yield.
- Increasing the initial reactor pressure increases the liquid product yield.
- Lowering the initial pH (acidic pH 1 - 2) of the flax straw suspension improves furfural yields, but, at the same time, it was found to accelerate undesired side reactions (pentanoic acid production).
- A solid acid catalyst (H-ZSM-5) was found to be highly selective towards the formation of furfural by improving furfural yield while suppressing undesired side products (carboxylic acids).
- Increasing the amount of H-ZSM-5 increases the yield of furfural.
• A solid acid catalyst is highly preferred for the current application due to its ease of separation and high selectivity.

• The highest carbon conversion (40%) was achieved at 325°C.

• The experimental results were used to derive an empirical power law rate model of the form 
  \[ -r_A = \frac{dX_A}{dt} = 8.3156 \times 10^{-1} e^{-\frac{27969.63}{RT}} (1 - X_A)^2. \]

• The activation energy and reaction order for the current process were found to be 28 kJ/mol and 2.0, respectively.

5.2 Recommendations

Based on the scope of the current work, the following recommendations can be made for further studies:

• Different kinds of heterogeneous acid catalysts could be tested to evaluate their performance for the current application. In depth characterization of the used solid acid catalyst should be done in order to elucidate the plausible reaction pathway and plausible deactivation pathway and develop plausible regeneration methods.

• Future studies could use LHHW and ER approaches to derive appropriate rate equations for each elementary step(s) proposed for the current process and accordingly propose the most plausible reaction pathway(s).
REFERENCES


APPENDIX A

Calculations of Yield and Conversion

The yield was calculated from the formula:

\[
\text{Yield of } \text{“A”} = \frac{\text{moles of } A}{\text{gram of flax straw used}} \left( \frac{\text{mol}}{\text{g}} \right)
\]

where “A” is the liquid or the gas product.

For the Liquid Product

Assuming ‘A’ represents the liquid product (phenol, furfural, formic acid, or acetic acid):

The integration of the peak from the GC-MS chromatograph corresponding to the compound (A) is done first. The GC-MS set integration parameters were:

- Initial Area Reject: 10
- Initial Peak Width: 0.299
- Shoulder Detection: off
- Initial Threshold: 20.0

The area obtained was plotted into the calibration curve for the compound ‘A’ to get the corresponding concentration in mg/L.

Below are the calibration curves for the four compounds
(a) Calibration Curve for Acetic Acid

\[ y = 1 \times 10^8 x \]
\[ R^2 = 0.9775 \]

(b) Calibration Curve for Formic Acid

\[ y = 7 \times 10^7 x \]
\[ R^2 = 0.9754 \]
(C) Calibration Curve for Phenol

(d) Calibration Curve for Furfural
Assuming a compound ‘A’ gave a concentration of 0.16877 g/L from the calibration curve:

Converting g/L to mg/mL gives 0.168775.

Also assuming 5 g of biomass was used and 95 mL of water:

Total amount (mg) in 95 mL = 0.168775 * 95 = 16.033606 mg.

This means, in 95 mL of water = 5 g of flax straw = 16.033606 mg of compound A.

From here, we can convert the compound ‘A’ to mg/g = (16.033606 mg) / (5 g)

= 3.206721 mg/g of flax straw.

If we know the molar mass of compound ‘A’, we can actually convert it to mol/(g of biomass).

**For the Gas Product**

The gas yield was calculated by multiplying the % fraction of the gas component from the GC chromatogram with the total volume of gas produced and then dividing it by the amount of biomass used for the reaction.

Example:

Assuming the % fraction of CO from the GC chart is 45%:

Volume of gas produced = 396 cc.
Volume fraction of CO = Mole fraction of CO = 0.45 \times 396 \text{ cc} = 178.2 \text{ cc} = 178.2 \text{ mol}

Assuming 5 g of flax straw was used:

Yield of CO = \frac{178.2 \text{ mol}}{5 \text{ g}}.

**Conversion:**

Conversion of Flax Straw (X_A): Flax straw conversion was calculated from CHNSO analysis (ultimate analysis) of the char remaining at the end of the reaction. The conversion was in terms of the amount of carbon remaining with respect to the amount initially present in the flax straw.

\[ \text{Carbon Conversion (Xc)} = X_A = \frac{W_{Ci} - W_C}{W_{Ci}} \]

where \( W_{Ci} = \) initial weight of carbon in the flax straw before the reaction.

\[ W_C = \) weight of carbon in the char at the end of the reaction. \]
APPENDIX B

Curve Fitting and Experimental Rate Calculations

The curve fitting for the Conversion Vs Retention time graphs shown in Figure 4.18 was done using a curve fitting tool called ‘Origin Pro. 8’. The equation for parabolic fit was used for the fitting, and a representation of these fittings is shown in the graph below for the three temperature points:

![Graph showing parabolic fit of Carbon Conversion (Xc) at 225°C](image)

Carbon Conversion at 225°C

<table>
<thead>
<tr>
<th>Equation</th>
<th>$y = A + Bx + Cx^2$</th>
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</thead>
<tbody>
<tr>
<td>Adj. R-Square</td>
<td>0.99756</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Carbon Conversion (Xc) at 225</th>
<th>Value</th>
<th>Standard Error</th>
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</thead>
<tbody>
<tr>
<td>A</td>
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<td>0.00763</td>
</tr>
<tr>
<td>B</td>
<td>0.00166</td>
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<tr>
<td>C</td>
<td>-7.61E-06</td>
<td>2.40E-06</td>
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</table>

<table>
<thead>
<tr>
<th>Carbon Conversion (Xc) at 225</th>
<th>Number of Points</th>
<th>Degrees of Freedom</th>
<th>Reduced Chi-Sqr</th>
<th>Residual Sum of Squares</th>
<th>Adj. R-Square</th>
<th>Fit Status</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4</td>
<td>1</td>
<td>5.89E-05</td>
<td>5.88E-05</td>
<td>0.99756</td>
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</table>
Carbon Conversion at 275°C

<table>
<thead>
<tr>
<th>Equation</th>
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<th>Carbon Conversion (Xc) at 275</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adj. R-Square</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Value</td>
<td>Standard Error</td>
</tr>
<tr>
<td>Carbon Conversion (Xc) at 275</td>
<td>A 0.2468</td>
<td>0.0068</td>
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</tbody>
</table>
Carbon Conversion at 325°C

<table>
<thead>
<tr>
<th>Equation</th>
<th>y = A + B'x + C'x^2</th>
<th>Value</th>
<th>Standard Error</th>
</tr>
</thead>
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<tr>
<td>Adj. R-Square</td>
<td>0.97546</td>
<td></td>
<td></td>
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<tr>
<td>Carbon Conversion (Xc) at 325</td>
<td>A</td>
<td>0.34338</td>
<td>0.00941</td>
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<tr>
<td>Carbon Conversion (Xc) at 325</td>
<td>B</td>
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<td>3.59E-04</td>
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<tr>
<td>Carbon Conversion (Xc) at 325</td>
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<td>-9.45E-06</td>
<td>2.90E-06</td>
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</table>

<table>
<thead>
<tr>
<th>Carbon Conversion (Xc) at 325</th>
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<tbody>
<tr>
<td>Number of Points</td>
</tr>
<tr>
<td>Degrees of Freedom</td>
</tr>
<tr>
<td>Reduced Chi-Sqr</td>
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<tr>
<td>Residual Sum of Squares</td>
</tr>
<tr>
<td>Adj. R-Square</td>
</tr>
<tr>
<td>Fit Status</td>
</tr>
</tbody>
</table>
Rate Calculations

Rate determination from the fitted curve was done by using a data analysis and modeling tool called ‘Tracker 4.0’ to find the slope (dX/dt) at each tangential point. The figure below shows a pictorial view of the software operating environment. The results obtained are shown in Table 4.2.
APPENDIX C

NLREG code with results for empirical rate model

The function below was used to regress the results given in Table 4.2 to determine the values of the parameters $A$, $E_a$, and $n$:

$$\ln \left( \frac{dX_A}{dt} \right) = \ln A - \frac{E_a}{RT} + n \ln (1-X_A) \quad \text{------------------------ (4.11)}$$

The code was written as follows:

Title "Parameter Estimation for Flax Straw Decomposition Rate Model":

Parameters $A$, $E$, $n$;

Variables $Y$, $X$, $T$;

Constant $R = 8.314$;

Function $Y = (A - (E)/(R*T)) + (n*X))$;

nplot;

where $Y = \ln \left( \frac{dX_A}{dt} \right)$, $A = \ln A$, $X = \ln (1-X_A)$

The result of the regression from the program (NLREG) is shown below:
Title "Parameter Estimation for flax straw decomposition rate Model";

Parameters A, E, n;
Variables Y, X, T;
Constant R =8.214;
Function Y = (A - (E/((R*T)) + (n*X));
npLOB;

Data;

Beginning computation...
Stopped due to: Both parameter and relative function convergence.

---- Final Results ----

NLREG version 6.3
Copyright (c) 1992-2005 Phillip H. Sherrod. All rights reserved.
This is a registered copy of NLREG that may not be redistributed.

Parameter Estimation for flax straw decomposition rate Model
Number of observations - 10
Maximum allowed number of iterations - 500
Convergence tolerance factor - 1.000000E-010
Stopped due to: Both parameter and relative function convergence.
Number of iterations performed - 7
Final sum of squared deviations - 5.3322684E-003
Final sum of deviations - 1.374900E-012
Standard error of estimate - 0.0275999
Average deviation - 0.0185878
Maximum deviation for any observation - 0.0422166
Proportion of variance explained (R^2) - 0.9882 (98.82%)
Adjusted coefficient of multiple determination (Ra^2) - 0.9849 (98.49%)
Durbin-Watson test for autocorrelation - 3.044
Analysis completed 24-Oct-2012 04:15. Runtime - 0.07 seconds.

---- Descriptive Statistics for Variables ----

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<th>Variable</th>
<th>Minimum value</th>
<th>Maximum value</th>
<th>Mean value</th>
<th>Standard dev.</th>
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<tr>
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<td>T</td>
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---- Calculated Parameter Values ----

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<th>Final estimate</th>
<th>Standard error</th>
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<th>Prob(t)</th>
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<td>0.00003</td>
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---- Analysis of Variance ----

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<th>Mean Square</th>
<th>F value</th>
<th>Prob(F)</th>
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