BIOMASS AND BIOENERGY 71 (2014) 381–393

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Catalytic subcritical water liquefaction of flax straw for high yield of furfural

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ARTICLE INFO

Article history:
Received 11 May 2013
Received in revised form
16 September 2014
Accepted 17 September 2014
Available online 8 October 2014

Keywords:
Flax straw
Linum usitatissimum
Acid catalysed liquefaction
Subcritical water
Furfural yield
Rate model

ABSTRACT

There is substantial interest in the application of biomass as a renewable fuel or for production of chemicals. Flax straw can be converted into valuable chemicals and biofuels via liquefaction in sub-critical water. In this study, the yield of furfural and the kinetics of flax straw liquefaction under sub-critical water conditions were investigated using a high-pressure autoclave reactor. The liquefaction was conducted in the temperature range of 175–325 °C, pressure of 0.1 MPa–8 MPa, retention time in the range of 0 min–120 min, and flax straw mass fraction (w_F) of 5–20 %. Also, the effect of acid catalysts on furfural yield was studied. The kinetic parameters of flax straw liquefaction were determined using nonlinear regression of the experimental data, assuming second-order kinetics. The apparent activation energy was found to be 27.97 kJ mol^{-1} while the reaction order was 2.0. The optimum condition for furfural yield was at 250 °C, 6.0 MPa, w_F of 5% and 0 retention time after reaching set conditions. An acid catalyst was found to selectively favour furfural yield with 40% flax straw conversion.

1. Introduction

Sustainability concerns and the continuous increase in the price of crude oil have amplified industrial interest for renewable chemicals and fuels. Biomass is an obvious choice to replace the petroleum feedstock. Not only does it provide a viable option to improve energy security, but also, it reduces greenhouse gas emissions and addresses the challenging problem of treatment of waste streams of process plants [1,2]. These researchers have reported that one attractive option to address these issues is the thermochemical conversion of lignocelluloses, with biomass being one of the most promising, as it offers the potential to serve as sustainable supply of fuels and chemical intermediates (e.g. aldehydes, acids, alcohols, etc.). The conversion of this material into valuable chemicals and biofuels thus offers a breakthrough in solving this challenging problem of treating waste stream that can pollute the environment while at the same time paving the way for newer energy resources. One option of converting this abundant lignocellulosic biomass into renewable fuel and chemical is the production of furfural.

Furfural is a key chemical for the production of furan (through catalytic decarboxylation) and tetrahydrofuran (through hydrogenation), thereby providing a biomass-based alternative to petrochemical production of these compounds [3]. Furfural is used primarily in lubricating oil refining and, in condensation with phenol, formaldehyde, acetone, or urea, to

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http://dx.doi.org/10.1016/j.biombioe.2014.09.017

produce resin with thermosetting properties and extreme physical strength. Furfural can serve as a precursor for the production of liquid alkanes (C_7–C_{15}) that serve as diesel fuel components [4,5]. Furfural is exclusively produced from lignocellulosic biomass by dehydrating pentoses (mainly xylose), which are present in significant amounts in the hemicelluloses of some agriculture residues and hardwoods [6]. Feedstocks for furfural production are the biomass with high pentosan content and as such, agricultural residues are usually preferred because they are homogeneous and readily available in large quantity from farming activities [5,6].

Flax (*Linum usitatissimum*) straw, a lignocellulosic biomass, is the fibrous stalk of the flax plant that is left in the field after the flax seed has been removed during harvesting [7]. Flax straw is used rather than tilled into the soil, primarily because of it strong fibre content. Canada is the largest grower and exporter of flax in the world [8]. Saskatchewan produces 70% of the total flax production in Canada [9,10]. 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. As a result, farmers traditionally manage flax straw by sinking it in windrows behind the combine or burning it after raking it into piles [8]. However, with this abundant flax straw [10], it is possible to generate renewable fuels and/or chemicals via different thermochemical processes, which will not only address this problem faced by farmers but also serve as a renewable energy source capable of adding to the supply of fuels and chemicals from the ones currently derived from fossil fuel.

On one hand, there is an immense potential in this lignocellulosic feedstock waiting to be explored, but on the other hand, lignocellulosic 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 [9,10]. Table 1 [11] compares the energy conversion efficiency of various processes existing today to convert wet biomass to value added products. From the table, 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. Lignocellulosic materials such as flax straw can be liquefied at low temperature and pressure in the presence of suitable solvent to produce biofuels, furfural, phenolic resins, carbon filter, etc.

Table 1 – Energy conversion efficiency for different biomass conversion processes.[a]

Moisture content in feed	5%	31%	55%	75%
Biomass conversion process	Energy conversion efficiency (%)			
Thermal gasification	61	55	47	27
Pyrolysis	57	53	45	27
Liquefaction	39	37	36	34
Anaerobic digestion	31	31	31	31
Sub/Supercritical water	55	55	55	55

[a] Yoshida et al. [11].

In some literature, phenol has been used as a solvent for biomass liquefaction in the presence of an acid catalyst (sulphuric acid, hydrochloric acid, phosphoric acid, oxalic acid, etc.) [12–17]. However using phenol as a liquefaction solvent could pose some concerns such as high cost, phenol recycling from the liquefied products, as well as some environmental concerns [13]. Organic solvents such as alcohols and cyclic carbonate have also been reported as being used as solvents for biomass liquefaction at low temperature [18–20]. Appell et al. [21] reported that woody biomass could be converted into 40–50% liquid products in the presence of CO with aqueous sodium carbonate as a catalyst under 28 MPa and 350 °C to 400 °C. Recently, there has been a strong interest in using hot-compressed and sub/supercritical fluid for biomass liquefaction. Biomass liquefaction in sub/supercritical water offers an attractive choice to eliminating the energy intensive drying process, especially when the moisture content is above 3.0% [22]. Compared to other biomass thermochemical processes, sub/supercritical water has high energy efficiency and can operate at a lower temperature, especially in the subcritical regime [23]. 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. Water at its critical point (374 °C and 22.1 MPa) has properties that are different from water under normal conditions. An example is the low dielectric constant, which is comparable with that of methanol or acetone under ambient condition, increasing ionic strength, and low viscosity which leads to better mass transfer and thus enhancing mass transfer limited chemical reactions [24–26].

A large volume of research work can be found in the literature on the supercritical water gasification of biomass and models of compounds such as cellulose and glucose [22,23,27], but only a few reports are available on the subject of subcritical water liquefaction in the literature [22–27]. This is because, in most studies on hydrothermal process, researchers have focused on the gaseous products, as supercritical gasification conditions favour gas formation in higher yields. This work focuses on product formation and yield optimization of valuable chemicals in the liquid phase. Also, the current study is the first of its kind to explore the potential of hydrothermal liquefaction of flax straw in subcritical water. In this study, a parametric study of the effect of temperature, pressure, flax straw mass fraction (w_F), (i.e. ratio of mass of flax straw per total mass of flax straw and water) and retention time on the yield of the solid products, gaseous products and four key compounds (formic acid, acetic acid, furfural, and phenol) in the liquid products have been investigated in the hydrothermal liquefaction of flax straw in subcritical water. The optimum condition to achieve the highest liquid and gas yield was also determined. To optimize the yield of furfural, a separate study was undertaken, where the effect of homogenous and heterogeneous acid catalysts was investigated. Finally, a kinetic modelling of flax straw conversion in subcritical water was performed in order to establish an empirical expression for the process. The results of the above–described investigation are presented and discussed in this paper.