Liquefaction of Corn Cobs with Supercritical Water Treatment

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Abstract

Corncob powder was liquefied in a high pressure reactor. The composition of the gas and liquid phases produced were analyzed. It was found that the yield of gas phase increased while the yields of solid and liquid phase decreased with increasing temperature. The gas phase was 2.5 - 7.7% (wt%), the liquid phase 87.8 – 95.5% (wt%), and solid phase 1.56 – 4.7% (wt%) at 300 – 375^{0}C. The gas phase consisted of hydrogen, carbon dioxide, carbon monoxide, alkane, and olefin. The liquid phase consisted of phenols, furanmethanol, and related derived compounds.

Keywords: Liquefaction; Corn cob; Supercritical Water Treatment

1. Introduction

Creating a cleaner environment and a more secure country are dual benefits of developing bio-based products, such as hydrogen fuels, chemicals, and bio-oils. There are a number of techniques that can directly use biomass as feedstock to produce energy and chemicals. These include fermentation of biomass to ethanol and gasification and pyrolysis of biomass to syngas and heavy oil. Federal agencies and private companies have invested heavily in research and development of these techniques. However, these techniques have limited commercial use because of high costs associated with the processes and/or limited knowledge of the processes and their products. Tremendous efforts have been made to convert lignocellulosic biomass to fermentable substrates to produce biofuels and chemicals. Xylan extracted from corn cob, which is an additive in pharmaceutical, printing and papermaking industry, was reported by Zdena et al.(1999) [1] Tsai et al. (2001) prepared activated carbon from corn cobs by using a combination of chemical and physical activation[2]. Rivas et al.(2002) prepared the fermentable hydrolysate by hydrolysis of corn cob[3].

However, information on the gases and the liquid chemicals produced by thermal chemical process is limited in the literature. The objective of this study was to investigate the feasibility of converting lignocellulosic biomass to sugars and burnable oil using supercritical water. Supercritical water condition can be created at high pressure. In our study, a Parr high pressure reactor was used. Process variables such as pressure, temperature, catalysts, solid load, and time were investigated. The products from the supercritical water assisted reactions are expected to consist of three phases: gaseous phase, liquid phase and solid phase. The yields and chemical and physical properties of individual phases will be determined.

2. Experimental

2.1. Materials

Dried corn cob, provided by Minnesota Agricultural Utilization Research Institute, was milled to 0.5 mm meals before liquefaction.

2.2. Apparatus and Process

The experimental apparatus includes a high pressure reactor (Parr 4575) and a recycle ice-water bath. The temperature of the reactor was controlled by a temperature controller. A known amount of corn cob was placed in the reactor, mixed with known amounts of water and KOH. The reactor was then sealed and purged with nitrogen gas at a flow rate of 80 ml/min in order to prevent secondary reactions such as thermal cracking and repolymerization. The reactor was heated to 300, 350, 375^0C at a heating rate of 10 K/min, and the desired temperature was held for 1 –10 min. After reaction, the gases were cool down and sampled using a gas bag by micro-GC analysis (Varian CP4900). The liquid condensed was collected into the sample bottle by GC-MS analysis (HP5890).

2.3. Chemical Analysis

The gaseous products were determined by gas chromatography with 3 packed columns (MS5A, PPQ and WAX) by using a thermal conductivity detector (TCD)for the analysis of CO,CO2, H2, CH4, C2H2,C2H6,C3H8 and so on. Volume concentration was calculated based on an external standard method.

Chemical compositions of the liquid products were identified by GC –MS using a DB5 capillary column (Hewlett –Packard).The GC was programmed at 60^0C for 0.5 min and then increased at 2.5^0C/min to 140^0C, and finally increased at 10^0C/min to 250^0C. The injector temperature was 300^0C and the injection size was 1 μl. The flow rate of carrier gas (Helium) was 0.6 ml/min. The ion source temperature was 250^0C for the mass selective detector. The compounds were identified by comparison with library spectra, the main compounds of which were confirmed by external standard compounds.

3. Results and Discussion

3.1.Effect of temperatures on yield

Figure1 shows the liquefaction rate of corncobs in subcritical and supercritical water at 10min. Corncobs, which usually were difficult to dissolve in water under ordinary temperature / pressure conditions, dissolved in supercritical water (374^0C, 22.1MPa) [4, 5]. In the condition of 300^0C, the liquefaction rate of corncobs was 68% only, while in the condition above 375^0C, over 82% of the corncobs was decomposed and liquefied in water after 10min supercritical treatment. In this study, we found the supercritical water extraction is appropriate for the treatment of ligneous biomass, to which any other technology under ordinary temperature / pressure conditions is difficult to apply, especially crop wastes that contains much water and is difficult to recycle.

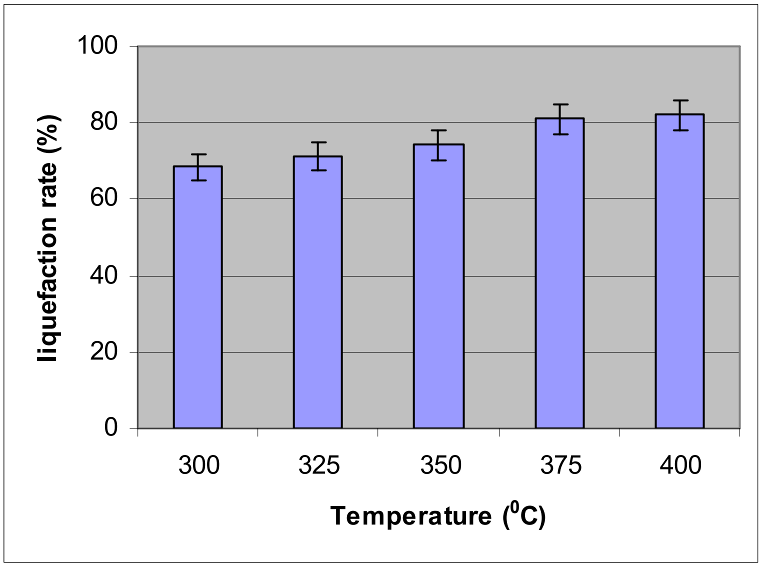


Figure 1. Liquefaction yield as a function of temperature (Liquefaction time 10min, corncobs content 10%, and no catalyst)

3.2 Effect of liquefaction times on yield

From Figure 2, we know liquefaction rate increases slightly as the increasing of liquefaction time. And after liquefaction process, gas part decreases as the increasing of liquefaction time. The yields of the gases, liquid and solid residue were 5.3 -7.7%, 87.8 – 90.9% and 3.7 – 4.4% at 5 – 20min, respectively.

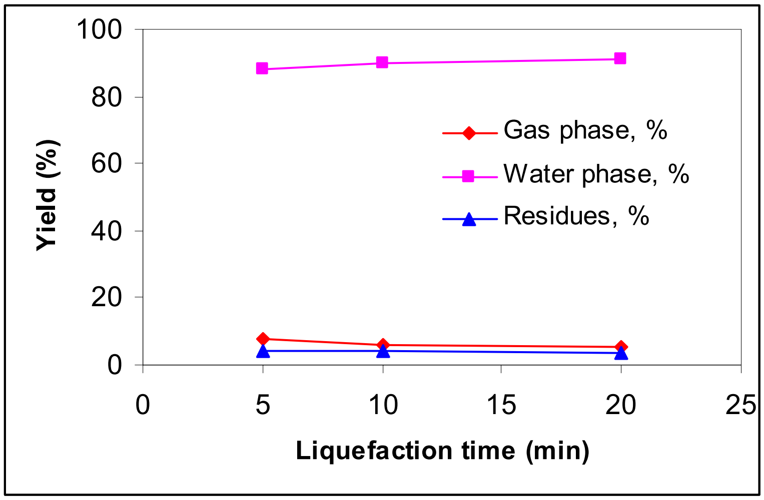


Figure 2. Liquefaction yield as a function of liquefaction time time (Liquefaction temp 350^0C, corncobs content 10%, and 5% KOH as catalyst)

3.3 Effect of KOH on yield

Adding some alkali into the corncobs solution could increase the liquefaction yield, as well as increasing the gas products' yield[6]. From Figure 3, we know liquefaction rate increases as the increasing of catalyst content. And after liquefaction process, gas part decreases as the increasing of liquefaction time. The yields of the gases, liquid and solid residue were 2.5 -7.7%, 87.8 – 95.5% and 1.56 – 4.7% at 1 – 15% KOH, respectively.

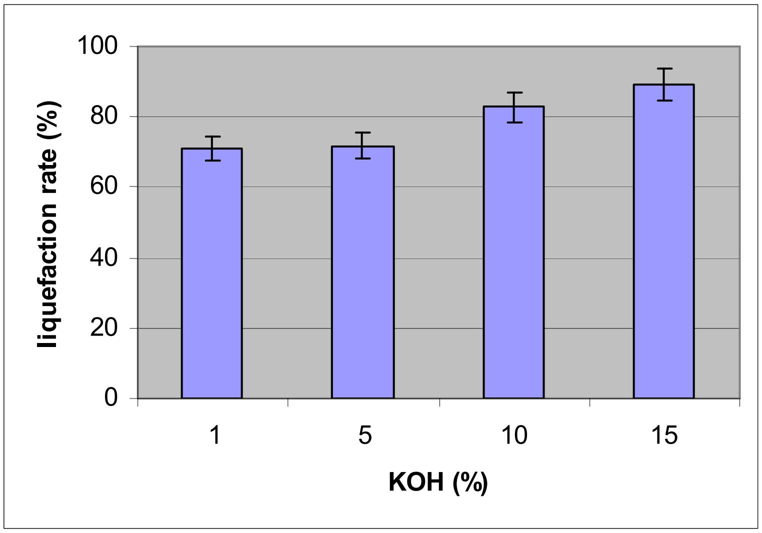
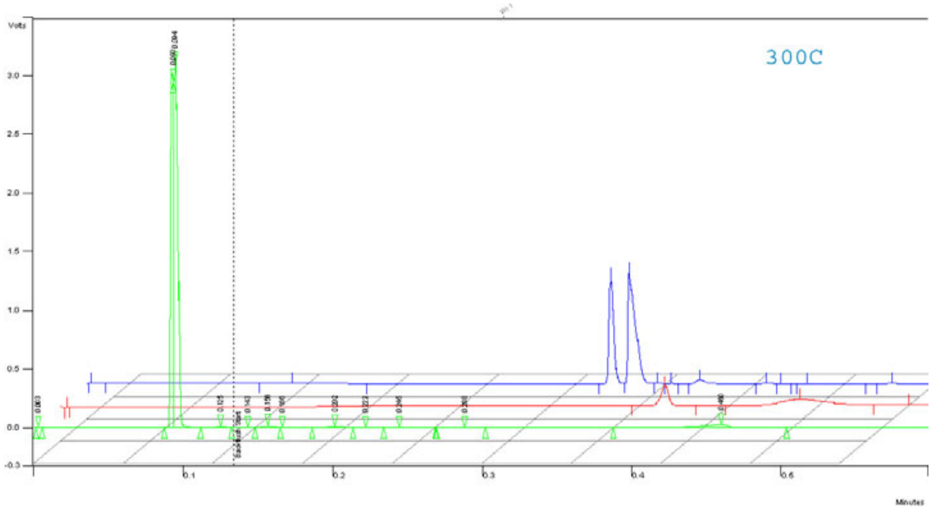
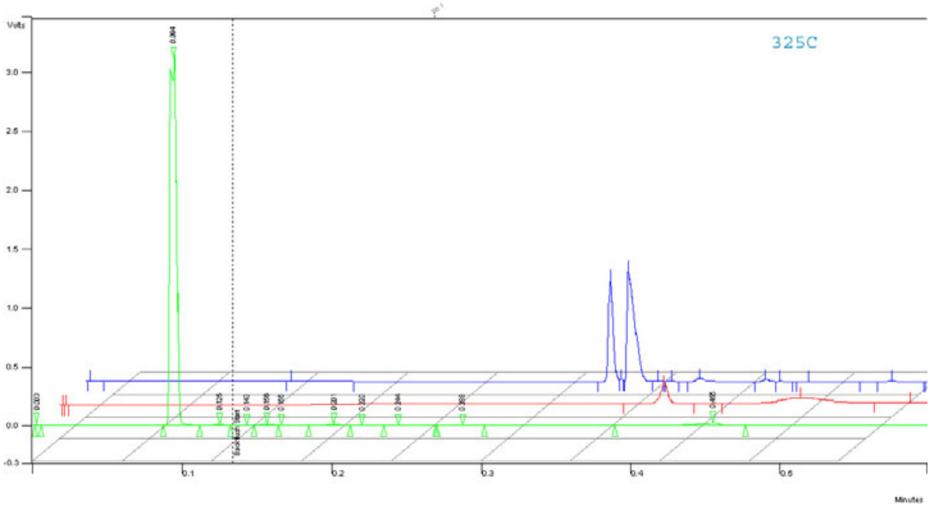


Figure 3. Liquefaction yield as a function of KOH content (Liquefaction time 10min, 10% corncobs, temp 350^0C)

3.4.Composition of the gaseous phase

The gases primarily consisted of hydrogen, carbon dioxide and carbon monoxide which account for nearly 40%(v/v) at 375^0C.Carbon dioxide and hydrogen may reach 31%(v/v) at 300^0C. The higher yield of carbon dioxide was closely related to the oxygenated functional group contained in the raw material which is easily broken, and formed more stable compounds than other functional groups.With increasing temperature, other components of the gas product included hydrogen, methane, ethylene and other olefin and alkine (Figure 4 and Table 1). The gases produced from high pressure liquefaction can be used to manufacture syngases.




325C
Volts
3.0
2.5
2.0
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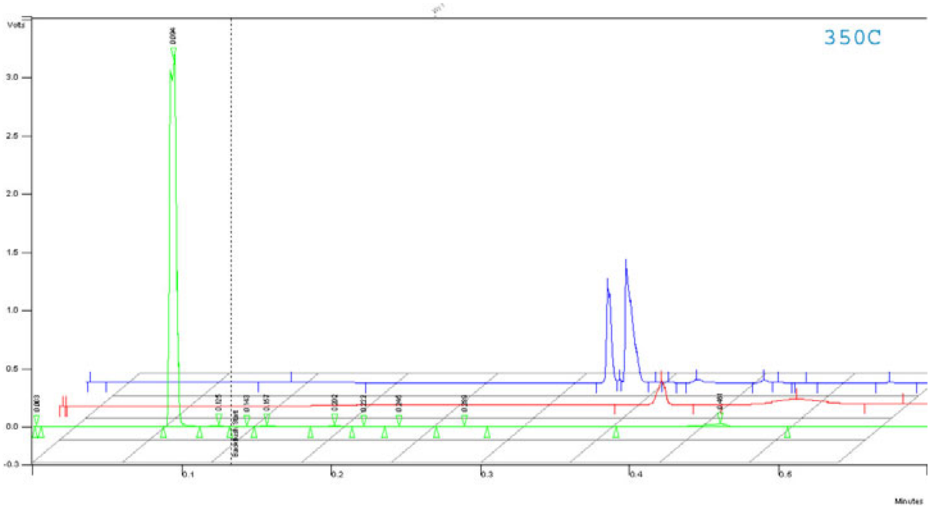
0.5
Minutes


350C
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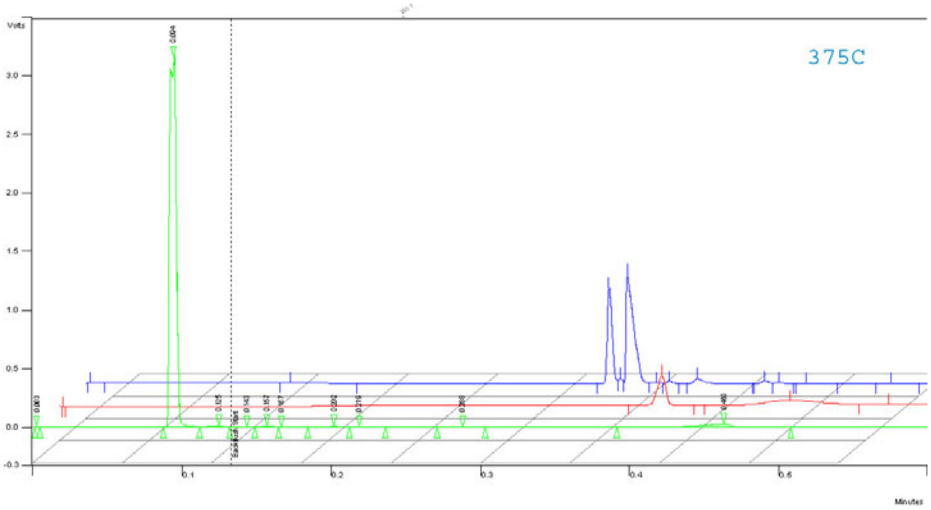
375C
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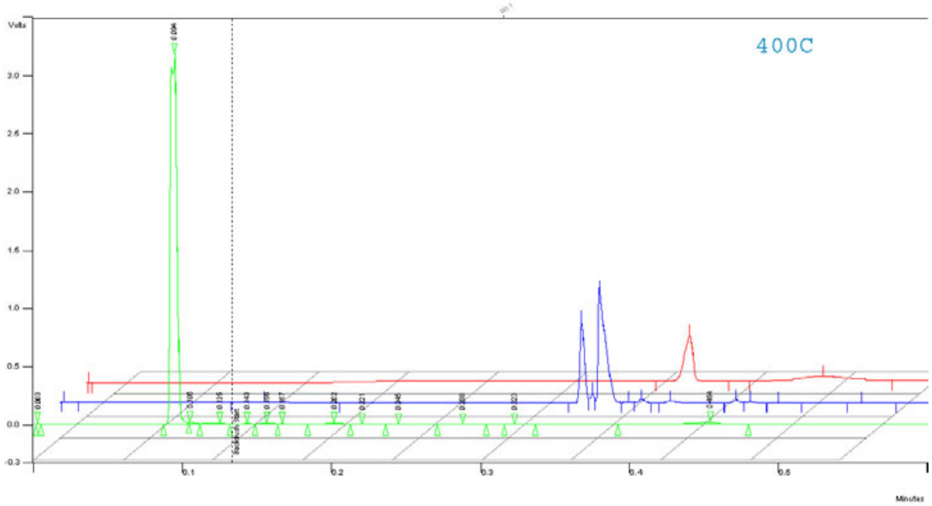


Figure 4 micro-GC chromatograms of the liquefaction gas obtained from corncobs. (Liquefaction time 10min, 10% corncobs, temp 300^0C, 325^0C, 350^0C, 375^0C, and 400^0C)

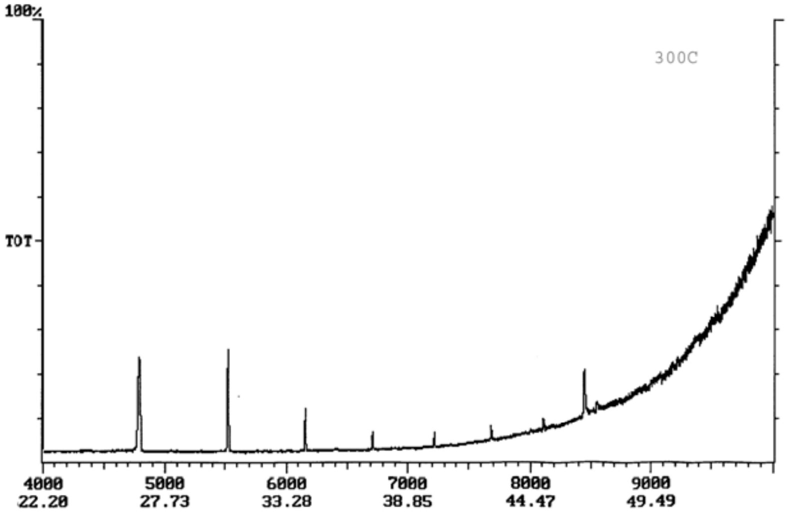
Table 1 Yield (% area) of the main gas compounds obtained from corncobs after 10 min reactions at designated temperatures.

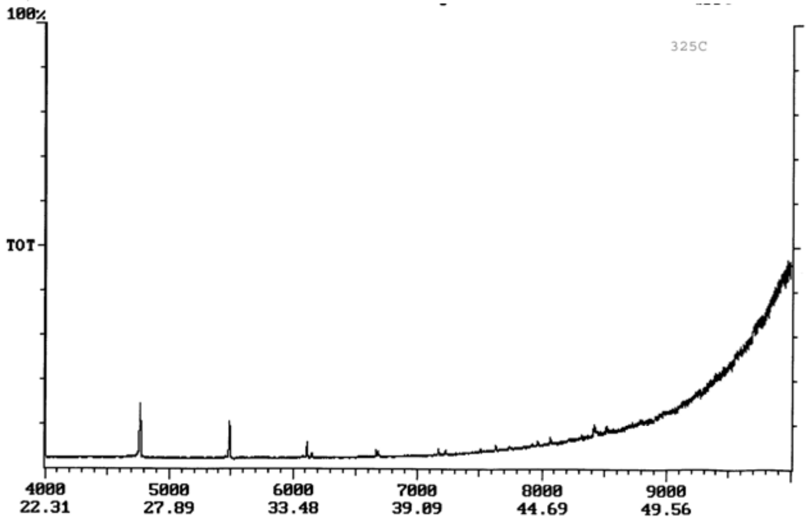
Product	**Temperature**				
	300^0C	325^0C	350^0C	375^0C	400^0C
H2	2.93	2.70	3.61	4.90	7.41
CO	7.78	8.09	8.74	7.76	6.33
CO2	28.6	23.55	24.4	23.3	24.0
C2H4	0.01	0.03	0.07	0.09	0.14
Acetylene	0.03	0.08	0.22	0.49	1.17
CH4	1.43	1.07	1.19	1.69	0.86
Ethane	0.01	0.01	0.01	0.41	0.02
Propane	0.11	0.09	0.06	1.17	0.09
Butane	0.01	0.01	0.01		0.03
Pentane			0.01	0.47	
Hexane	0.19	0.28	0.31	0.19	0.33

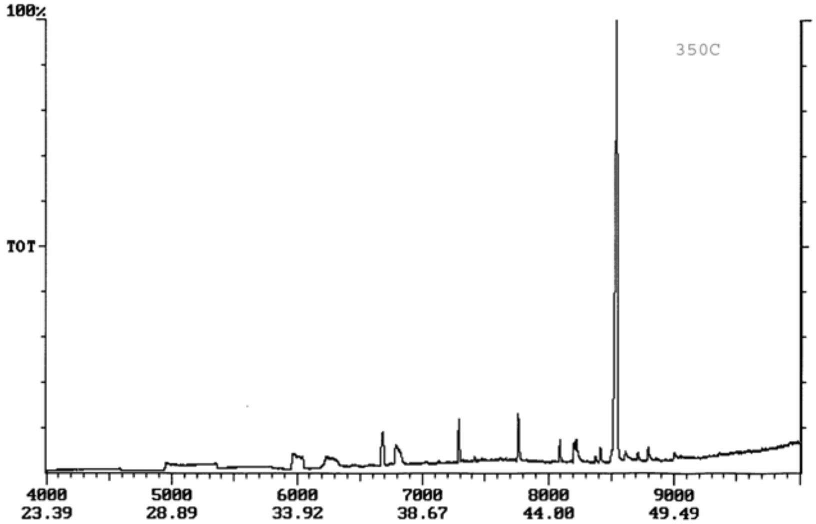
3.5. Composition of the liquid phase

The analysis of the chemical characteristics of the liquid could help determine how the liquid could be used or further refined to produce value added chemicals, additives and fuels[7]. Our results showed that the liquefaction liquid was mainly composed of oxygenated compounds such as phenols, furans and other derivatives. Those derivatives were useful for chemical industries. For example, phenols have wide applications in organic chemistry such as synthesis of formaldehyde resin, dyes and medicines. Furanmethanol is an excellent solvent and can be used for producing furfuran resin.

Phenol, 2-hydroxy-2-cyclopenten-1-one, 2-methyl-cyclopentene-1-one, 2-furanmethanol, etc. were detected in the GC-MS analysis. The composition of the liquid varied with temperatures. The amount of the compounds with branched chains increased as the temperature was increased, which may be attributed to secondary reactions occurring under high temperature conditions, suggesting that product yield and characteristics could be controlled through controlling the reaction temperature.







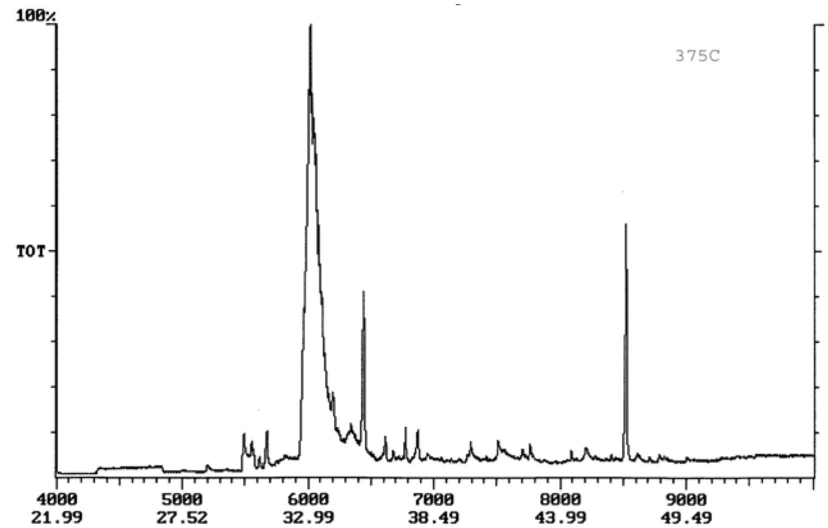


Figure5 GC-MS chromatograms of the liquefaction oil obtained from corncobs. (Liquefaction time 10min, corncobs content 10%, temp 300^{0}C, 325^{0}C, 350^{0}C, and 375^{0}C).

4. Conclusions

Corncobs could be nearly completely liquefied in supercritical water after about 30 min at 375^{0}C with addition of 10% potassium hydroxide. The reactions under supercritical water condition produced gases, chemicals dissolved in liquid and solid residues. The gas phase was 2.5 -7.7% (wt%), the liquid phase 87.8 – 95.5% (wt%), and solid phase 1.56 – 4.7% (wt%) at 300 – 375^{0}C. The gas products are mainly composed of H2, CO2 and CO, approximately 45%(v/v) of the total gas phase, and small amount of olefin and alkine. The major components of the liquefaction liquid are phenols, furanmethanols and related derived compounds. The liquid phase can be used either directly as asoxygenated fuel, or as feedstock for further chemical refining process, opening a huge window of possibilities for biomass utilization.

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