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Optimization of Process Variables on Supercritical Liquefaction of Giant Fennel

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ABSTRACT

Milled giant fennel (*Ferula orientalis* L.) stalks were treated in supercritical solvents in the presence of catalyst in a high pressure reactor. Effects of process variables including temperature (from 240 to 320 °C), solvent (2-propanol, 2-butanol, and acetone), catalyst (Na_2CO_3, NaOH, and $ZnCl_2$), particle size (from 0.224>Dp>0.150 to 0.850>Dp>0.425), solvent/mass ratio (from 50/5 to 50/15) and reaction time (from 45 to 95 min) on product yields were investigated. The amounts of solid, liquid and gas produced, as well as the properties of the resulting bio-oils were determined. Temperature, catalyst and reaction time were major factors affecting the product yields and composition of bio-oils. The highest conversion (liquid+gas products) of 73.48% was achived in acetone with 10% zinc chloride at 320 °C. Acetone as solvent, zinc chloride (10%) as catalyst, 0.224>Dp>0.150 as particle size, 50/5 as solvent/mass ratio, 80 minutes as reaction time provide the optimum conditions for the supercritical liquefaction of *Ferula orientalis* L. The liquid products (bio-oils) obtained at 300 °C were analyzed by gas chromatography–mass spectrometry (GC-MS). The bio-oils which contained higher amount of carbon and hydrogen than that of the original raw material had higher heating values ranging from 23.66 to 26.17 MJ/kg.

***Keywords**:* Biomass, Thermochemical process, Liquefaction, Particle size, Catalyst.

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1. Introduction

The term biomass refers to wood, short-rotation woody crops, agricultural wastes, short-rotation herbaceous species, wood wastes, bagasse, industrial residues, waste paper, municipal solid waste, sawdust, biosolids, grass, waste from food processing, aquatic plants and algae animal wastes, and a host of other materials. The basic structure of biomass consists of three organic polymers: cellulose, hemicelluloses, and lignin in the trunk, foliage, and bark. [1] Recently, energy from biomass resources has received remarkable attention due to the increasing worldwide energy requirements, and the demand for biofuels has rapidly increased in the recent decades. Biofuels can be broadly defined as solid, liquid, or gaseous material consisting of or derived from renewable biomass resources. [2-4]

Thermochemical liquefaction is one of the potential conversion processes to produce biofuels from biomass. In recent years, of thermochemical liquefaction processes, supercritical fluid extraction method has attracted much more attention than other methods as it is environmental friendly and could be performed at relatively lower temperatures (250-400 °C) depending on the critical temperature and pressure of the used organic solvent. A fluid is called as supercritical when its temperature and pressure goes higher than its critical pressure and critical temperature which shows the end of the liquid-vapour coexistence curve and distinct liquid and gas phases do not exist any more. A supercritical fluid can effuse through solids like a gas, and dissolve materials like a liquid. Supercritical fluids have liquid-like properties such as the lower density of the liquid and gas like properties such as lower viscosity and higher diffusivity. These unique properties make them powerful solvents for mass transfer rates of reactants to biomass molecules and easily penetrate the fibrous solids. They have the ability to dissolve compounds that are not normally soluble in either liquid solvents or gases so that the efficiency of liquefaction reactions can significantly be promoted.[5,6]

Biomass feedstocks, such as wood, agricultural and forest residues, energy plants, urban and solid industrial wastes, lumber and municipal wastes have attracted great attention as renewable energy sources in the worldwide. Turkey has high potential of agricultural renewable source with diverse crops production in 25 million hectares of arable land. [7,8] One of them called *Ferula* is a genus of about 170 species of flowering plants in the family Apiaceae, native to the Mediterranean region east to central Asia, mostly growing in arid climates. The plant is perennial; stem stout, smooth, cylindrical, hollow and it grows up to 3 m. The leaves are hairless, shiny, glaucous, finely divided into numerous thread-like lobes and prominent sheathing bases. The lower leaves have long stalks, the upper leaves with a shorter stalk, eventually much reduced to sheaths clasping them with the stem. The yellow flowers, produced in large umbels appear during March and June, which are umbrella-shaped inflore-scences/bunches of flowers. The large umbels are seeds flattened, large, about 15 mm long, striated due to numerous resin canals and with thin lateral wings. [9,10]

As one of the abundant and fast growing plants found in many parts of Turkey, *Ferula orientalis* L. has been chosen with the idea of liquid fuel or chemical feedstock production from its stalks which go dormant by midsummer and no value in terms of industrial respect. The main purpose of the present work was investigation and optimization of process variables including temperature, solvent, catalyst, particle size, solvent/mass ratio and reaction time on supercritical liquefaction of giant fennel by extending the previously published study. [10] The liquid products obtained at 300 ^{o}C were analyzed by GC–MS. The elemental compositions and higher heating values (HHV) of liquid products were also determined.

2. Materials and methods

2.1. Materials

Ferula orientalis L. samples were collected from Ağrı region (geographical coordinates: 39 36' 32" North, 42 59' 21" East) of Turkey. It was harvested in spring, dried in open air and ground in Perten Instruments LM120 mill to pass through a screen of 0.224 mm aperture and extracted with petroleum ether (b.p. 40-60 ^{o}C) in a Soxhlet extractor for 8 h.

The proximate and ultimate (elemental) analyses of raw material were performed before liquefaction experiments and the results are given below. Ultimate analysis; carbon: 44.72%, hydrogen: 6.07%, nitrogen: 0.75% and oxygen: 48.46%. Proximate analysis; lignin: 26.11%, cellulose: 41.28%, hemicellulose: 22.57%, moisture: 5.66%, ash: 4.85%, soxhelet extractives: 0.87% as percent of dry feedstock. Tappi test methods [11] were used for determining the contents of lignin (Tappi T222), cellulose (Tappi T202), ash (Tappi T211) and moisture (Tappi T264). Hollocellulose content was determined using the chloride method. [12]

2.2. Experimental procedure

The experiments were conducted in a 75 mL capacity cylindrical high pressure reactor (autoclave) made of stainless steel with dimensions of 30 mm inner diameter, 60 mm outer diameter and 145 mm height. [7,8,10] The reactor is designed to operate at maximum temperature of 360 ^{o}C and a maximum pressure of 30 MPa. The liquefaction experiments were performed in five series. In the first one, experiments were performed without catalyst at five different temperatures (240, 260, 280, 300 and 320 ^{o}C) with 0.224-0.150 mm sample with 2-propanol, 2-butanol and acetone. In catalytic experiments, the desired quantity of the catalyst (2 wt%, 5wt%, 10wt%) was dissolved first in the solvent and then added to reactor. Catalytic experiments were performed with three different catalysts (sodium carbonate, sodium hydroxide, zinc chloride) at a constant temperature of 300 ^{o}C to investigate the effect of catalysts on liquefaction yields with three different ratios. Third group of experiments were performed to determine the effect of particle size on product yields. Three more particle diameter (Dp) (0.850>Dp>0.425, 0.425>Dp>0.300, 0.300>Dp>0.224) samples were used in liquefaction experiments at 300 ^{o}C in addition to the ones performed with 0.224>Dp>0.150 particle size sample. In the first three series, 10 grams of sample and 65 mL of solvent were used at all runs. Fourth group of experiments were performed to determine the effect of solvent/mass ratio (from 50/5 to 50/15) on product yields at 300 ^{o}C constant temperature with all solvents without catalyst.

The reactor was heated to desired reaction temperature by an external jacket heater at a constant heating rate of 10 ^{o}C/min and hold at this temperature for 75 min. During the liquefaction, the reaction temperature was measured with a thermocouple and controlled at 240±5, 260±5, 280±5, 300±5 and 320±5 ^{o}C. Upon completion of the reaction, the reactor was cooled to room temperature by putting in cold ice-water mixture. After cooling, the reactor was opened, uncondensed gases were vented and then the contents (unconverted raw material and liquids) of the reactor were poured into a 200 mL beaker for separation. The residual oils and solids inside the reactor were washed several times with the used solvent until all of them are recovered. The liquid phase was filtered in 20 mL glass crucible to separate the solid (unconverted raw material) from the mixture. The solid was washed several times with distilled water to remove the impurities. The pre-weighed crucible and solid were dried to constant weight in an oven at 105 ^{o}C. The filtrate was evaporated under reduced pressure by rotary evaporator system at 40-50 ^{o}C temperatures to recover the liquids. This fraction was weighed and designated as liquid. The conversion of raw material to liquid and gasesous products was calculated by subtraction of amount of solid left behind in the reactor with considering the moisture and ash content. The amount of gas evolved was calculated by subtraction of amount of solid and liquid products from amount of initial raw material. The fifth and last group of experiments were performed to determine the effect of reaction time ranging from 45 to 95 min in addition to 75 min at 300 ^{o}C with constant solvent/mass ratio of 50/10 with acetone only.

The conversion and product yields were calculated using the following equations:

$$\text{Conversion (\%)} = \frac{(W_{\text{Biomass} \;\;,\text{db}} - W_{\text{Solid} \;,\text{db}})}{W_{\text{biomass} \;\;,\text{db}}} \text{ x100} \qquad (1)$$

$$\text{Liquid yield (wt \%)} = \frac{(W_{\text{Liquid}})}{W_{\text{Biomass} \;\;,\text{db}}} \text{ x100} \qquad (2)$$

$$\text{Solid yield (wt \%)} = \frac{(W_{\text{Solid} \;,\text{db}})}{W_{\text{Biomass} \;\;,\text{db}}} \text{ x100} \qquad (3)$$

Gas yield (wt %) = 100% – liquid yield (wt %) –solid yield (wt %) (4)

where $W_{\text{Biomass, db}}$ and $W_{\text{Solid, db}}$ are the weights of initial biomass and remaining solid respectively on dry basis. Fig.1. shows the liquefaction of giant fennel and sequence of separation of product mixtures into individual fractions.

The liquid products (4 samples) obtained at 300 ^{o}C were analyzed and characterized by elemental and GC-MS analysis. Elemental analyses were performed using LECO CHNS-932 analyzer. The GC-MS analysis was performed on Agilent GC-MS 7890A/5975C series (Agilent Technologies, Santa Clara, CA). The column (HP –INNOWAX, length: 60m., I.D.: 0,250 mm, film: 0,25 μm and temperature limits: from 40 ^{o}C to 260 ^{o}C) and injector temperatures were the same as those for GC. The carrier gas was helium at a flow rate of 1.7

ml/min. Samples of 1 μL were injected with a split ratio of 1:30. The GC oven temperature program was as follows: started at 40 °C; held for 10 min, raised from 40 °C to 200 °C with 5 °C/min heating rate; held for 15 min, raised to 240 °C with 10 °C/min heating rate; held for 15 min, raised to 260 °C with 10 °C/min heating rate; held at this final temperature for 10 min. The column was directly introduced into the ion source of an Agilent 5975 series mass selective detector operating with an electron impact (EI) ionization mode. Chemical constituents were identified by comparison of their retention indices with literature values [13,14] and their mass spectral data with those from the Wiley7n.1, ADAMS.1 and NIST05a.L mass spectral databases.

3. Results and discussion

3.1. Conversion yields

The conversion scheme of biomass to liquid and gaseous products was given in a previous study. [15] According to literature [16], liquefaction of ligno-cellulosic materials such as *Ferula orientalis* L. depends on its chemical composition which is mainly composed of lignin, cellulose and hemicellulose as they have different liquid formation temperatures. Yields of conversion were increased with temperature and catalyst percent. According to results, the highest conversion of 64.32% was obtained at 320 °C temperature in non-catalytic runs with 46.87% liquid. As for catalytic runs, the highest yield of 73.48% was obtained at 300 °C by using 10% zinc chloride with 53.97% liquid product.

The conversion yields of experiments performed with woody plants are generally low as they have high percentage of lignin. The percentages of lignin in leafy trees, needle leaf trees are 20–25% and 25–35% respectively. On the other hand, these values are 23–32% for dicotyledons and 17–23% for monocotyledons (Typha, corn and bamboo). Therefore, conversion with plants containing less lignin is greater than others. [7]

3.2. Effect of temperature on product yields

It is obvious that biomass or other lignocellulosic materials pyrolyze at a high temperature and the thermolysis effects increase with temperature. Since the intermolecular kinetic energy increases with temperature, which speed up the molecules in the system to decompose due to the decrease of energy barrier for intermolecular interactions. The widely acceptable essence of direct liquefaction of biomass was summarized as follows: firstly, the weak chemical bonds in the biomass, such as C–O–C or C–C were pyrolyzed to form some large free radical fragments which can be terminated by hydrogen or other smaller fragments to form the so-called preasphaltene and asphaltene (PA + A); secondly, the PA + A was converted into oil and gas. All these steps must be conducted at high temperature, thus, the temperature is the most important factor during liquefaction. [8,17]

The effect of temperature on product yields is given in Fig. 2 which shows the experimental runs at different temperatures ranging from 240 ^{o}C to 320 ^{o}C used for all organic solvents without catalyst for 75 minutes holding time. As seen from Fig. 2 that temperature has a positive effect either slightly or sharply on both conversion and liquid yields. For example, yield of conversion has increased from 32.77% to 46.21% in 2-propanol medium when temperature is increased from 240 ^{o}C to 320 ^{o}C. As expected, yields of conversion have increased for all solvents in all runs. Similar pattern is observed for liquid yields. In fact, temperature is a critical parameter for supercritical organic solvent conversion. The trend of liquid yield against temperature is consistent with the data in literature. In the literature, there are similar reports indicates that the increasing of liquid yield with increase in temperature in liquefaction of biomass. [18,19]

Thermal decomposition of biomass begins at 200–300 °C, and CO, CO_2, H_2 and H_2O are vaporized as gas. Thermal decomposition is a heat generating reaction which is a characteristic phenomenon of biomass. When wood is heated, there is an attack on the glycosidic linkages, that leads to dehydration, decarboxylation, decarbonylation and cleavage of the molecules into smaller fragments that are soluble; and finally, gaseous compounds are formed. Lignin reactions include fragmentation of a and b ether linkages and carbon–carbon bond cleavage, leading to the formation of soluble and gaseous products. [8,20]

3.3. Effect of solvent on product yields

When we look at both non-catalytic and catalytic runs, it was found that the most effective solvent for conversion of *Ferula orientalis* L. is acetone at all temperatures. The maximum yield of conversion of 64.32% was obtained with acetone at 320 ^{o}C in the non-catalytic runs. Acetone is followed by 2-butanol as the second most effective solvent with 53.26% of conversion yield at 320 ^{o}C. 2-propanol was the least effective among all solvents except at 240 ^{o}C. The yield of conversion obtained by 2-butanol is lower than others at 240 ^{o}C. This is because of the critical temperature of 2-butanol which is greater than 240 ^{o}C indicating that it was not in supercritical condition at that temperature.

Acetone is an excellent supercritical solvent because of dipole moment (acetone: 2.91D, 2-propanol: 1.66 and 2-butanol: 1.62D) and boiling point. The potential advantage of using a supercritical fluid reaction medium is that it may be possible to increase the selectivity of a reaction while maintaining high conversions. The reactants and catalyst can dissolve in a single fluid phase so that the reaction occurs homogeneously. Labile reaction products may be more readily isolated from the reaction mixture by adjusting the pressure or temperature to induce a phase split, thus avoiding unwanted side reactions. [21-23]

Many studies have been conducted on the effect of solvent to liquefaction yield. It has been found that the lowest solid residue content is obtained by using simple alcohols such as methanol, ethanol, propanol and butanol. Higher alcohols as well as organic acids result in much higher solid residue contents. However, the disadvantage of the simple alcohols is their relatively low evaporation point. They basically evaporate before the biomass is liquefied. [21,23]

3.4. Effect of catalyst on product yields

The effect of catalyst and catalyst ratio on conversion and liquid yields is shown in Fig. 3. Catalytic liquefaction experiments were carried out at constant temperature of 300 °C to determine both effect of catalyst (Na_2CO_3, NaOH and $ZnCl_2$) and catalyst ratio (2, 5, 10%) on the product yields. As seen from Fig. 3, catalysts had different effects on product yields. Among them, zinc chloride was the most effective one which increased the yields with increasing ratio in all solvents. For example, the conversion has increased from 61.74% without catalyst to 73.48% with 10% $ZnCl_2$ in acetone and from 50.15% without catalyst to 61.89% with 10% $ZnCl_2$ in 2-butanol. The conversions have increased steadily with zinc chloride catalyst and increase of catalyst ratio in all solvents and reached its maxiumum value of 73.48% with 10% ratio in acetone. Sodium carbonate and sodium hydroxide catalysts have shown similar effects in all solvents, decreasing the conversions in all solvents with increasing ratio. When compared with each other, sodium hydroxide was more effective than sodium carbonate. That is, decreases in conversions with sodium hydroxide were greater than sodium carbonate in all solvents. For example, the conversion has decreased from 50.15% without catalyst to 46.90% with 5% NaOH in 2-propanol, but with sodium carbonate, the conversion has decreased from 50.15% without catalyst to 47.25% with 5% Na_2CO_3 in 2-propanol. The catalytic results may be explained according to solubility of used catalysts. Since zinc chloride is well soluble in all solvents, it may have been efficient and increased the conversions. Another reason for the effectiveness of zinc chloride is that it has ability of hydrogen transfer. On the other hand, as sodium carbonate and sodium hydroxide are not well soluble in the solvents used in this study, they had negative effect and decreased the conversions. So, it can be concluded that sodium carbonate and sodium hydroxide may have acted as inhibitors in the solvents used in this study. The results obtained with sodium carbonate and sodium hydroxide in 2-butanol and acetone are consistent with our previous studies. [7,8,15,23]

Concerning the catalytic effect of alkalies (Na_2CO_3 and K_2CO_3), there has been little description about the roles that a catalyst plays in the liquefaction with some exceptions. Appell et al. proposed the mechanism for sodium carbonate-catalyzed liquefaction of carbohydrate in the presence of carbon monoxide. [24,25] According to literature, alkali salts such as sodium carbonate and potassium carbonate can act as catalysts for hydrolysis of macromolecules, such as cellulose and hemicellulose, into smaller fragments if water and simple alcohols such as methanol and ethanol are used as supercritical solvent. The micellar-like broken down fragments produced by hydrolysis are then degraded to smaller compounds by dehydration, dehydrogenation, deoxygenation and decarboxylation. Once produced, these compounds rearrange through condensation, cyclization and polymerization, leading to new aromatic compounds. [26,27] when cellulose was thermochemically converted in an alkali solution. They suggested that these aromatic compounds were formed by condensation or cyclization of unstable intermediate fragments which were generated by degradation of cellulose. [15,28]

3.5. Effect of particle size on product yields

The effect of particle size on conversion and liquid yields is shown in Fig. 4 which indicates that change in particle size effected product yields significantly. According to Fig. 4, when particle size was decreased, product yields (conversion, liquid and gas) were increased. For example, when particle size was decreased from 0.850>Dp>0.425 mm to 0.224>Dp>0.150 mm, the conversion was increased from 41.06% to 46.21% (11.25% increase) in 2-propanol at 300 ^{o}C. Accordingly the solid yields were increased with increasing particle size of the sample while the liquid yields were decreased. This was because of insufficient heat and mass transfer due to the large diameter of the particles, which in turn, caused lower reaction rates. Similar results were obtained in 2-butanol and acetone. It can be concluded from results that 0.224>Dp>0.150 mm particle size samples are the most suitable for obtaining high liquid yields from liquefaction of *Ferula orientalis* L.

These results are consistent with the previous studies reported in literature, that is, increase in particle size leads to greater temperature gradients inside the particles and the core temperature of the particles are lower than the surface which causes higher solid yield and lower liquid and gas yields. [10,29,30] Particle size is known to influence pyrolysis and liquefaction yields. This can be explained in terms of heating rate and mass transfer limitation. The heat flux and the heating rate are higher in small particles than in large particles. Larger particles will heat up more slowly, so the average particle temperatures will be lower and hence volatile yields is expected to be less. If the particle size is sufficiently small, it will be heated uniformly. The higher heating rate favors a decrease of the solid yield.[31,32]

Effect of particle size on product yields was investigated only for pyrolysis of various biomass species in the literature. However, there is not much research regarding the effect of particle size for supercritical liquefaction of biomass. Shen et al. [33] explained the decrease in liquid yield with increasing biomass particle size in terms of biomass cellular structure. It is proposed that the cell structure may affect the pyrolysis behaviour of biomass, such as the release of alkaline or alkaline earth metallic species. In the preparation of small biomass particles ranging between 0.18–0.6 mm by using a cutting mill, much of the cellular structure of biomass is destroyed. The diffusion of pyrolysis products which were formed inside wood cells are affected seriously by cell walls. The increase of intensity of secondary reactions in the closed cells may cause to decrease in the yield of liquid yield.

3.6. Effect of solvent/mass ratio on product yields

Effect of solvent/mass ratio on product yields was investigated by conducting reactions at constant temperature of 300 ^{o}C with changing the solvent/mass ratio from 50/5 to 50/15. Variation of solvent/mass ratio was realized by changing the amount of raw material from 5 to 15 gram in 2.5 increments with constant amount of solvent (50 mL). Effect of solvent/mass ratio on conversion and liquid yields is given in Fig.5. As seen from Fig.5, both conversion and liquid yields were increased with increasing solvent/mass ratio and the values were obtained with 50/5.

The conversions in 2-propanol, 2-butanol and acetone were steadily increased from 40.37 to 46.34%, from 43.26 to 49.24% and from 53.84 to 60.82% respectively as the solvent/mass ratio were increased from 50/15 to 50/7.5. Further increase in solvent/mass ratio had almost no effect on conversion. Similar trend was observed in liquid yields. For example, the liquid yields in 2-propanol were increased from 31.64% to 35.71% as the solvent/mass ratio was increased from 50/15 to 50/7.5. Further increase of solvent/mass ratio to 50/5 slightly increased the liquid yield (36.12%). The highest liquid yield of 45.86% was obtained in acetone with 50/5 ratio which indicates that acetone was not only a solvent but also a reactant and incorporated into the bio-oil during liquefaction.

The results show that supercritical organic solvent can play an important role in degradation of lignocellulosic biomass in terms of diffusion and penetration into the solid particles. At lower solvent/mass ratios, the raw material can not form a well-mixed suspension in the reactor because of the limited amount of solvent. This would result in unfavorable mass and heat transfers which limit the solvolysis and liquefaction reactions inside the reactor, thus reducing the conversion and liquid yields. At higher solvent/mass ratios, on the other hand, the raw material can mix well with the solvent. This would increase the mass and heat transfers, thus increasing the conversion and liquid yields. Ionic and radical reactions take place and intermediate products are formed during liquefaction of biomass. When amount of solvent is increased, the concentration of these intermediate products is diluted. This will lower the possibility of the formation of cross-linked and reverse reactions between intermediate products, thus increasing conversions and liquid yields. [34,35]

3.7. Effect of reaction time on product yields

Many studies have been performed regarding the effect of reaction time on liquefaction of biomass. Duration of reaction time can define the conversion of biomass and composition of resulting products. Optimization of reaction time is necessary for effective decomposition of biomass components. [36,37] The effect of reaction time on liquefaction of *Ferula orientalis* L. was performed at 300 °C using acetone with solvent/mass ratio of 50/10 by varying the reaction time from 45 to 95 min in addition to 75 min. Effect of reaction time on product yields is given in Fig.6. The conversions and liquid yields were increased steadily until 80 min with increasing the reaction time and then started to decrease again. As shown in Fig.6, the liquid yield was increased from 34.89 to 44.23% as the reaction time was increased from 45 to 80 min. Further increasing the reaction time has decreased the liquid yields due to the increasing chances of the secondary and tertiary reactions of liquids suggesting that they have reached their saturation point at reaction time of 80 min. The solid yields were decreased with increasing the reaction time and reached the lowest value of 39.96% at 80 min. Further increase in reaction time has gradually increased the solid yields possibly due to the tar formation from condensation or repolymerization of liquid products. [34] During biomass degradation, decomposition, dehydration and condensation reactions occur simultaneously. The results indicate that decomposition reactions were dominant at shorter residence time (<85 min) while condensation reactions became significant at longer residence. Therefore, 80 min would be suitable as a reaction time for degradation of *Ferula orientalis* L. at 300 °C. [38]

3.8. Characterization of liquid products by Elemental and GC-MS analysis

The results of elemental analysis and higher heating values of liquid products are given in Table 1. The Dulong formula was used to estimate higher heating values of liquid products. As seen in Table 1, the liquid products have higher carbon and lower oxygen contents than raw material. The higher heating values of liquid products were bigger than 23.66 MJ/kg and significantly higher than that of the raw material (16.15 MJ/kg). [39-43]

The total ion chromatograms of four liquids obtained in at 300 ^{o}C are given Figs. 7-10. The list of identified compounds in Figs. 7-10 is given in Tables 2-5 respectively. As seen from Tables 2-5, liquids produced by degradation of biomass components; hemicellulose, cellulose and lignin contains many types of compounds having different molecular structures and molecular weights. These compounds are composed of mainly five groups: monoaromatics, oxygenated compounds, nitrogenated compounds, polyaromatic compounds and their derivatives. Monoaromatics include benzene and derivatives, toluene, furans, phenols and derivatives. Aliphatics are mainly composed of alkanes, alkenes and their derivatives while oxygenated compounds contain aldehydes, ketones, esters and carboxylic acids. Amines and amides such as pyridine, pyrimidine and pyrazole are classified as nitrogenated compounds. Lastly, polycylic aromatic compounds such as anthraquinone and naphthalene and derivatives were identified by GC-MS analysis. The number and types of compounds obtained in liquid products were in accordance with the yields obtained in solvents. As seen from Figures 5-8, even though using different solvents and different catalysts, the same retention characteristics of compounds from gas chromatographic capillary column at the same intervals (22-32 min) were obtained. The most number of compounds (56) was obtained in acetone with zinc chloride as they are the most effective solvent and catalyst. However, similar compounds such as acids and esters have been produced in 2-propanol and 2-butanol which have similar structures and acted as not only solvents but also reactants in liquefaction.

4. Conclusion

In this study, a waste biomass, *Ferula orientalis* L. stalks were converted to liquid and gas products by the degradation under supercritical conditions at temperatures from 240 to 320 ^{o}C in a high-pressure reactor. The effects of liquefaction variables such as temperature, solvent, particle size, catalyst, solvent/mass ratio and reaction time on product yields were investigated. In both the non-catalytic and catalytic runs, acetone was found to be the best solvent for liquefaction of *Ferula orientalis* L. at all temperatures. Smaller particle size, higher solvent/mass ratio, shorter residence time gave higher yields and zinc chloride as catalyst was more effecive than others. As as result, acetone as solvent, zinc chloride (10%) as catalyst, 0.224>Dp>0.150 as particle size, 50/5 as solvent/mass ratio, and 80 minutes as reaction time provide the optimum conditions for supercritical liquefaction of *Ferula orientalis* L. In conclusion, thermochemical degradation of *Ferula orientalis* L. stalks is a promising process to produce liquids with higher heating values and/or value-added chemicals.

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Figure Captions

Figure 1 Procedure for liquefaction and sequence of separation of products into individual fractions

Figure 2 Effect of temperature on product yields

Figure 3 Effect of catalyst on conversion and liquid yields

Figure 4 Effect of particle size on conversion and liquid yields

Figure 5 Effect of solvent/mass ratio on conversion and liquid yields

Figure 6 Effect of reaction time on product yields

Figure 7 The total ion chromatogram of the liquid product obtained with 2-propanol as solvent and 10% Na_2CO_3 as catalyst at 300 ^oC

Figure 8 The total ion chromatogram of the liquid product obtained with 2-butanol as solvent and 10% NaOH as catalyst at 300 ^oC

Figure 9 The total ion chromatogram of the liquid product obtained with acetone as solvent and 10% $ZnCl_2$ as catalyst at 300 ^oC

Figure 10 The total ion chromatogram of the liquid product obtained with 2-butanol as solvent and 10% $ZnCl_2$ as catalyst at 300 ^oC

Table 1 The results of elemental analyses[a] and higher heating values of liquid products in Figs. 4-7.

Elemental	2-Ppropanol+Na_2CO_3	2-Butanol+NaOH	Acetone+ZnCl	2-Butanol+ $ZnCl_2$
Carbon	59.34	58.24	62.71	59.17
Hydrogen	7.08	6.96	7.14	7.21
Nitrogen	1.22	1.07	0.55	0.98
Oxygen[b]	32.36	33.73	29.60	32.64
H/C molar ratio	1.43	1.43	1.36	1.46
O/C molar ratio	0.40	0.43	0.35	0.41
HHV (MJ/kg)	24.45	23.66	26.17	24.53

[a] Weight percentage on dry and ash free basis. [b] By difference

Table 2 List of Identified Compounds in Figure 7

Number	Time (min)	Compound	% area
1	21.64	6-Methyl octahydro coumarin	1.17
2	22.01	Methyl ester of N-methyl carbamic acid	1.09
3	23.23	2-Cyclopenten-1-one, 3-methyl-	1.28
4	23.51	4-Hydroxy-3-hexanone	3.25
5	23.81	Hydroxymethapyrilene	0.86
6	24.55	Acetic acid	23.89
7	26.01	Propanoic acid	3.22
8	26.49	Bicyclo [2.2.2] octane	1.40
9	27.14	n-Propylmaleamic acid, 1-methylethyl ester	1.88
10	27.32	2-Furancarboxylic acid, 1-methylethyl ester	1.31
11	27.79	Furan, 2,5-dimethyl-	24.46
12	27.92	Thiazole, 2-ethoxy-	3.46
13	28.06	Cyclohexanol, 3,5-dimethoxy-, stereoisomer	2.47
14	29.46	3,4,4-D3-3-Hydroxy-cyclopentene	1.21
15	30.09	3H-Pyrazol-3-one, 2,4-dihydro-4,5-dimethyl-	0.58
16	30.53	2-Amino-4-methyl-3-pyridinol	5.90
17	32.47	Phenol	1.19
18	34.59	1-Tetradecene	1.02
19	38.32	Thiophene, 2-[(methylthio) ethynyl]	15.05
20	38.44	Decane, 1,2-epoxy-	0.53
21	39.48	3-Methylbutanal	0.33
22	43.47	Toluene, 3,4,5-trimethoxy-	1.25
23	43.79	2-Pyrimidinamine	0.66
24	43.81	4-Hydroxy pyridine	1.49
25	59.91	Anthraquinone, 1-ethoxy-	0.82
26	67.22	Cinnamic acid, p-(trimethylsiloxy)-, methyl ester	0.22

Table 3 List of Identified Compounds in Figure 8

Number	Time (min)	Compound	% area
1	3.89	1-Propene, 2-methyl-	0.53
2	4.27	2-Pentanol, 2,4-dimethyl-	0.36
3	5.82	Methyl ethyl ketone	3.24
4	6.62	Formic acid, 1-methylpropyl ester	2.14
5	7.53	Acetic acid, 1-methylpropyl ester	7.32
6	7.64	2-Propanone, O-methyloxime	14.17
7	9.66	3-Octanol	1.23
8	9.96	Propanoic acid, 1-methylpropyl ester	3.05
9	15.13	n-Butyl alcohol	35.02
10	23.53	2-hexylfuran	1.34
11	24.01	Hydrazinecarboxylic acid, 1,1-dimethylethyl ester	0.72
12	24.19	Hexane, 3-ethyl-2,5-dimethyl-	0.76
13	24.67	N,N-Dimethylhydrazine	0.65
14	25.21	4-Hydroxy-3-hexanone	1.23
15	25.37	Ether, tert-butyl isopropyl	1.23
16	25.51	Methyl 2-methylbutanoate	1.64
17	27.60	Isobutyl isopentanoic acid ester	1.76
18	27.87	2-Furanmethanol	1.38
19	28.42	4-Methylaminobutanoic acid	0.71
20	30.13	Dibutyl succinate	2.23
21	30.58	Phenol, 2-methoxy-	1.52
22	30.74	Pentanamide, N-ethyl	0.59
23	31.48	Dibutyl glutarate	4.48
24	33.13	Phenol, 4-ethyl-2-methoxy-	4.34
25	38.41	3-Pyridinamine, 2,6-dimethoxy-	2.08
26	41.27	Phenol, 2-methoxy-4-(1-propenyl)- (Z)-	1.40
27	41.56	Propanoic acid, 2-methyl-, butyl ester	1.56
28	41.82	Butanoic acid, butyl ester	2.15
29	56.98	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	1.17

Table 4 List of Identified Compounds in Figure 9

Number	Time (min)	Compound	% area
1	11.27	2-Pentene, 4,4-dimethyl-, (Z)-	0.52
2	14.62	3-Penten-2-one, 4-methyl-	38.31
3	20.08	Mesitylene	34.80
4	21.11	Phenol, 2-methoxy-4-methyl-	0.08
5	23.04	Propanenitrile, 3-(ethylamino)-	0.61
6	23.71	1,5-Heptadien-4-one, 3,3,6-trimethyl-	0.36
7	24.03	Benzenemethanol, 3-amino-	0.11
8	24.45	Acetic acid	0.76
9	25.48	2-Cyclopenten-1-one, 3,4-dimethyl-	0.15
10	25.57	1,3-Benzenediol, 4-propyl-	0.54
11	25.73	2,5-Heptadien-4-one, 2,6-dimethyl-	2.76
12	25.93	Naphthalene, 1,2,3,4-tetrahydro-5,6-dimethyl-	1.48
13	26.13	2-Cyclopenten-1-one, 3-methyl-	0.20
14	26.38	1-(methylthio)-1,3-butadiene	0.08
15	26.47	Spiro [2.4] heptan-4-one	0.16
16	26.71	3,5-Dihydroxy toluene	0.06
17	26.97	2,5-Diethyl furan	0.10
18	27.02	Glycocyanidine	0.21
19	27.18	4-Methoxy-2,5-dihydro toluene	0.23
20	27.39	Isophorone	2.17
21	27.49	Benzene, 1,3,5-trimethyl-2-(1-methylethenyl)-	4.45
22	27.69	(exo)-6-Methylbicyclo [3.2.0] heptan-2-one	0.37
23	27.79	Benzofuran, 2,3-dihydro-2,2,4,6-tetramethyl-	0.91
24	28.04	Acetophenone	0.22
25	28.15	9-Borabicyclo [3.3.1] nonane, 9-(3-methoxycyclohexyl) oxy-	0.30
26	28.47	Ethanone, 1-(2-methylphenyl)-	0.17
27	28.69	3,4-Dihydroxyacetophenone	0.10
28	28.72	Phenol, 3-(dimethylamino)-	0.07
29	29.15	Benzaldehyde- 3,5-dimethyl-	0.14
30	29.41	4-acetyl-1,5-dimethylpyrazole	0.20

31	29.59	S (-); R (+) -3-Phenylbutan-1,3-diol	0.45
32	29.86	2,4-Cyclohexadien-1-one, 4,6-dimethyl-6-(2-propynyl)-	0.07
33	30.09	Ethanone, 1-(2,4-dimethylphenyl)-	0.46
34	30.22	Benzene 1-(2-butenyl)- 2,3-dimethyl-	0.86
35	30.38	2,4,6-Octatriene, 2,6-dimethyl-	0.11
36	30.53	Phenol, 2-methoxy-	0.32
37	30.64	Ethanone, 1-(2,4,6-trimethylphenyl)-	0.66
38	30.75	Benzene, 1-(1,1-dimethylethyl)-2-methoxy-3-methyl-	1.01
39	30.94	2-methylene-3-methyl-9-hydroxy-3-decalin	0.20
40	31.09	Naphthalene, 1,2,3,4-tetrahydro-6,7-dimethyl-	0.54
41	31.29	Benzene, 1,4-dimethyl-2-(2-methylpropyl)-	0.42
42	31.78	p-Xylene, 2-ethyl-	0.08
43	31.93	2-Heptanone, 6-methyl-6-[3-methyl-3-(1-methylethenyl)-1-cyclopropen-1-yl]-	0.35
44	32.28	3,5,7,7-Tetramethylcycloocta-2,4-dien-1-one	0.03
45	32.47	Phenol	0.18
46	32.65	2-Cyclohexen-1-one, 5,5-dimethyl-3-(2-methylpropenyl)-	0.11
47	32.79	Pyridine, 2,4,6-trimethyl-	0.56
48	33.18	3,4-Dimethyl (1H) pyrrole, 2-[(3,4-dimethyl-[2H]-pyrrol-2-ylidene) methyl]-	0.68
49	33.56	Ethanal, 2-methyl-2-[4-(1-methylethyl) phenyl]-	0.29
50	33.98	Cresol <meta->	0.17
51	34.45	Tetracyclo [5.3.1.1 (2,6).0 (4,9)] dodecane, 11-methoxy	0.16
52	35.56	2-Acetylthiophene	0.22
53	35.79	Dimethyl phenol <2,6->	0.38
54	37.24	1 (2H)-Naphthalenone, 3,4-dihydro-3,3,6,8-tetramethyl-	0.81
55	38.32	Phenol, 2,6-dimethoxy-	0.09
56	66.39	Ethanone, 1-(3-hydroxyphenyl)-	0.18

Table 5 List of Identified Compounds in Figure 10

Number	Time (min)	Compound	% area
1	3.89	1-Propene, 2-methyl-	4.25
2	4.27	4-O-Acetyl-2,5-di-O-methyl-3,6-dideoxy-d-gluconitrile	1.98
3	5.11	4-Ethyl-4-heptanol	19.55
4	5.21	5-Amino-1,2,4-thiadiazole	25.86
5	5.84	3-Methoxy-1-propene	4.90
6	7.48	Acetic acid, 1-methylpropyl ester	4.35
7	7.68	Acetic acid, 1-methylpropyl ester	6.33
8	10.09	Propanoic acid, 1-methylpropyl ester	15.30
9	23.29	2,4-Dimethylfuran	0.72
10	23.46	Propanamide, N-ethyl-	0.48
11	23.53	Uridine, 2'-deoxy-, 3',5'-bis(trifluoroacetate)	0.41
12	23.71	Acetaldehyde, di-sec-butyl acetal	0.41
13	23.85	1,3-Dioxolane, 2-ethyl-2-isobutyl-	0.51
14	24.03	1-(1-Methoxypropoxy) butane	2.12
15	24.21	Dibutyl sulphite	1.67
16	24.64	Acetic acid	0.74
17	25.22	1-Ethoxy-3-pentanol	1.40
18	25.37	3-Methoxy butan-2-ol	1.07
19	25.52	Propanoic acid, butyl ester	1.00
20	27.60	2-Furanmethanol, tetrahydro-, acetate	1.25
21	28.42	4-Methylthiazole	1.19
22	28.53	2-Furancarboxylic acid, 2-pentyl ester	0.58
23	30.13	Butanedioic acid, dibutyl ester	1.91
24	30.58	Mequinol	0.61
25	31.48	Butanedioic acid, methyl-, bis(1-methylpropyl) ester	0.54
26	38.41	Phenol, 2,6-dimethoxy-	0.87

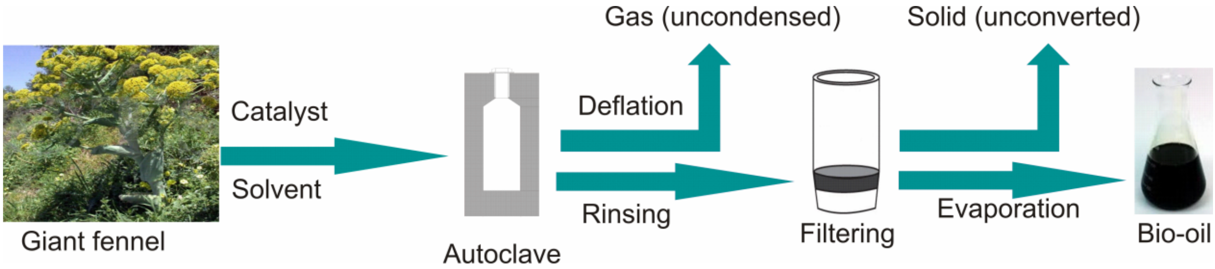
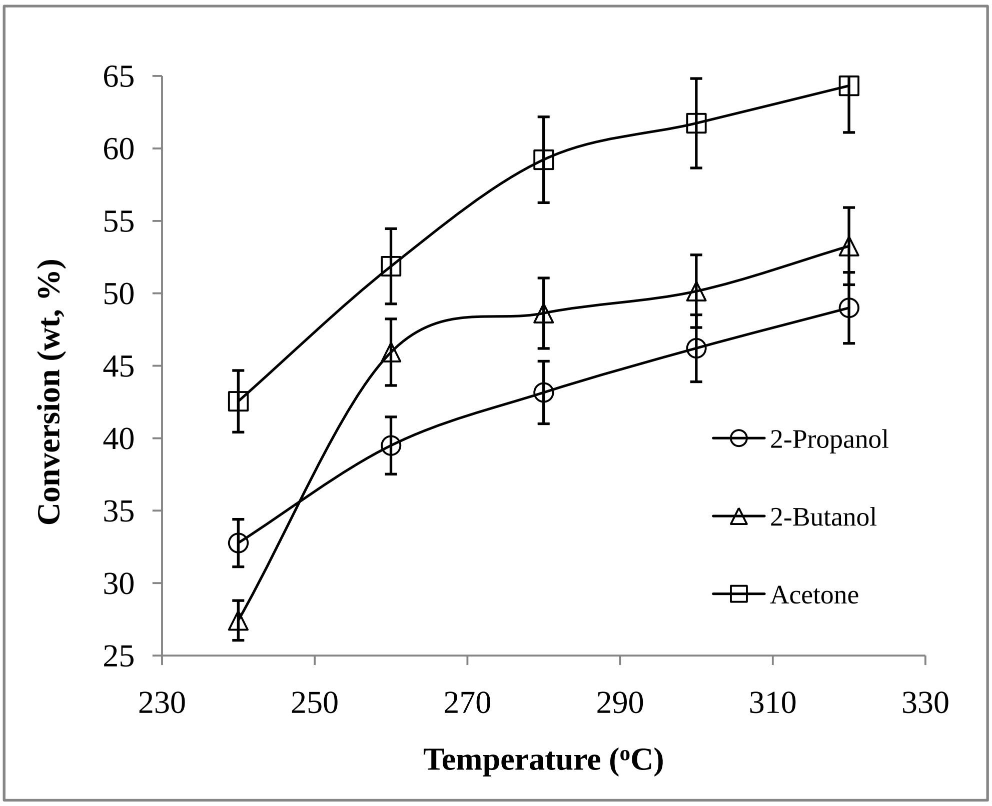
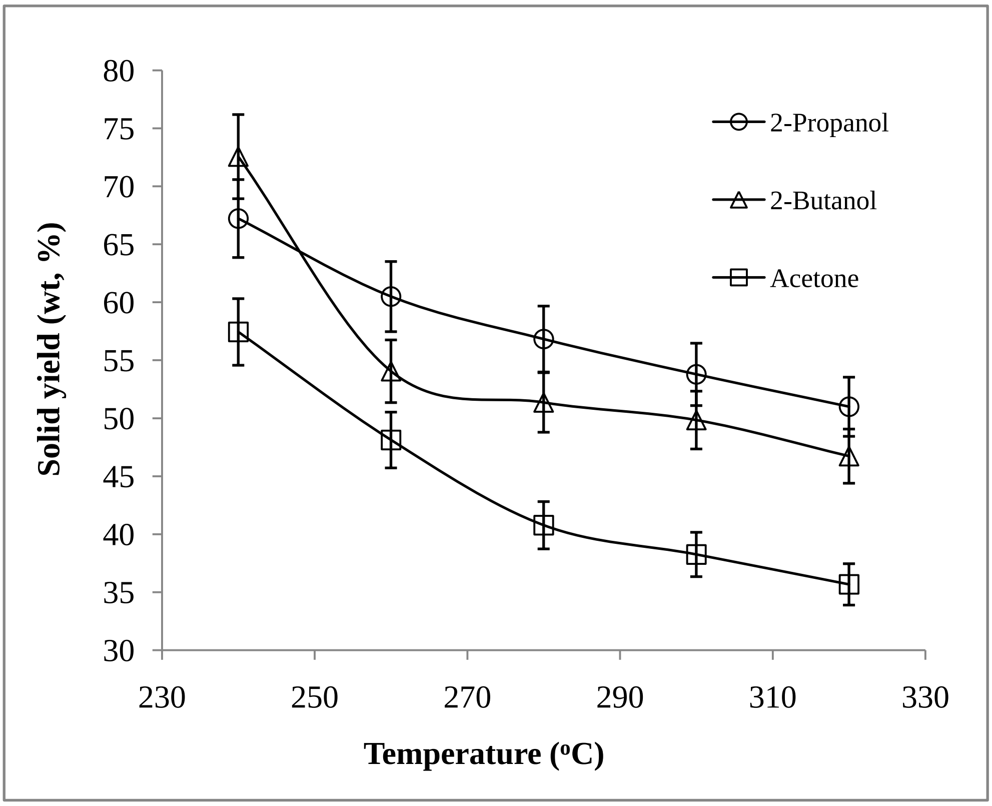


Figure 1 Procedure for liquefaction and sequence of separation of products into individual fractions


65
60
55
50
45
40
35
30
25
Conversion (wt, %)
230
250
270
290
310
330
Temperature (°C)
2-Propanol
2-Butanol
Acetone


80
75
70
65
60
55
50
45
40
35
30
Solid yield (wt, %)
230
250
270
290
310
330
Temperature (°C)
2-Propanol
2-Butanol
Acetone

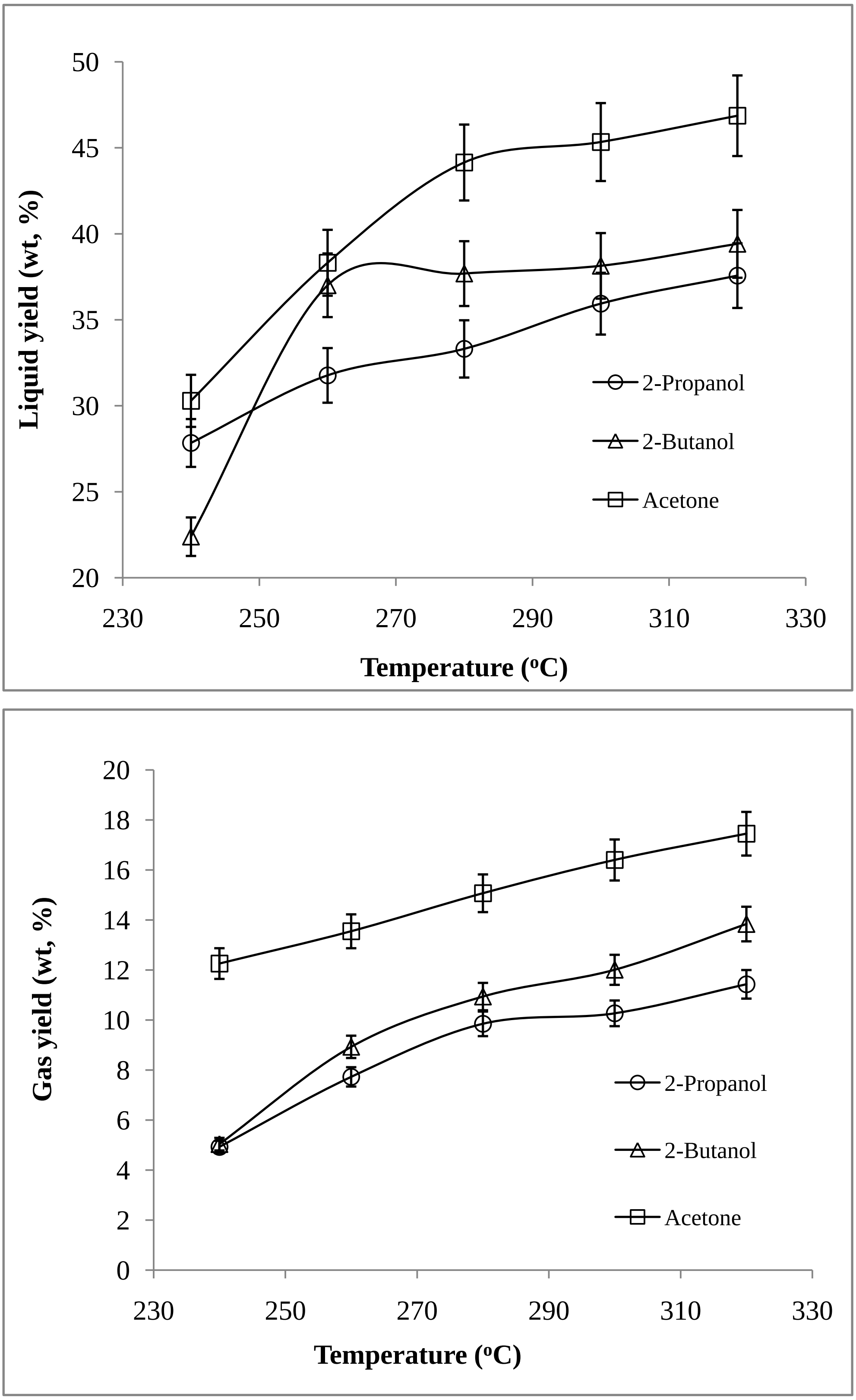
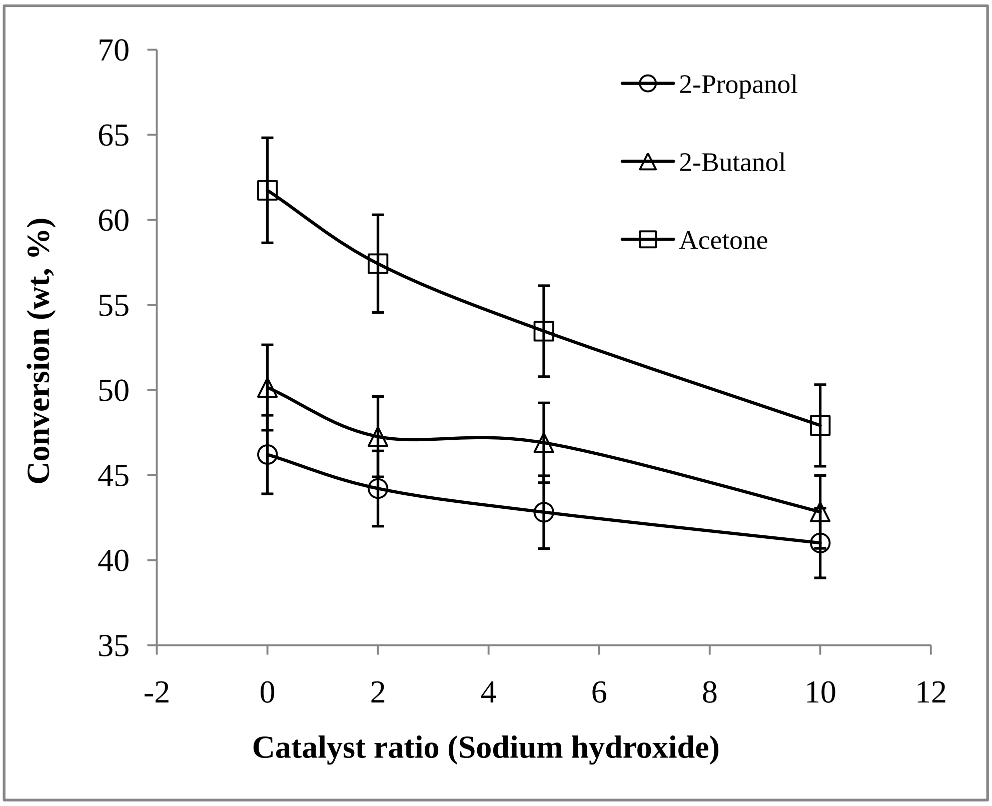
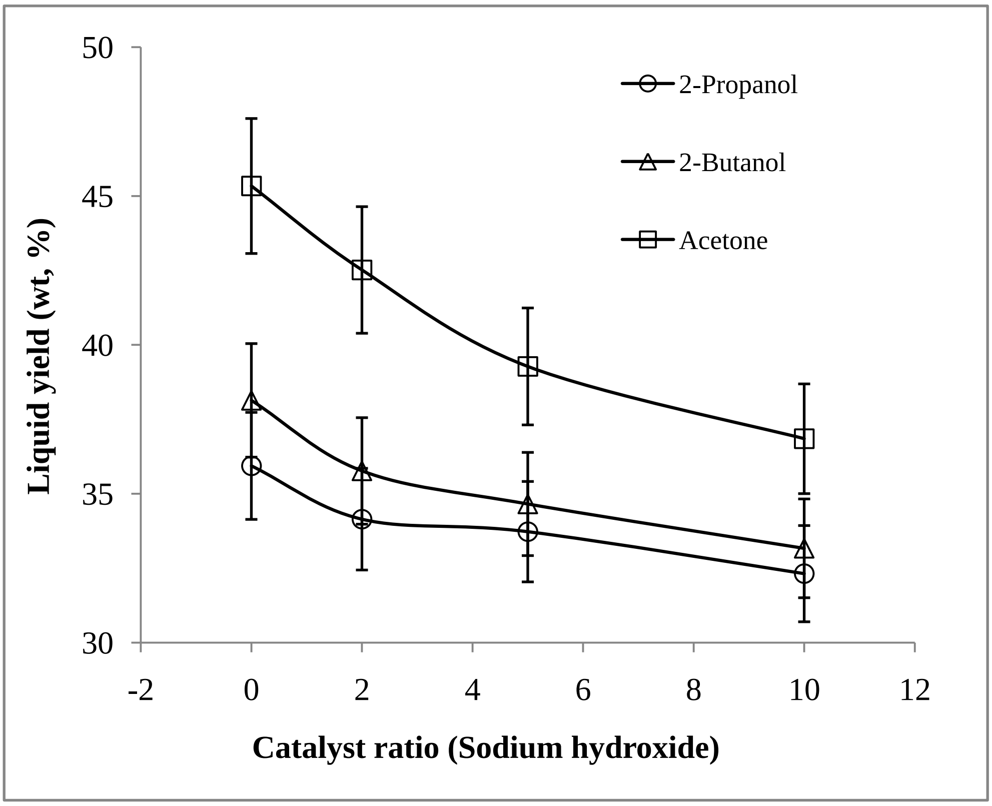
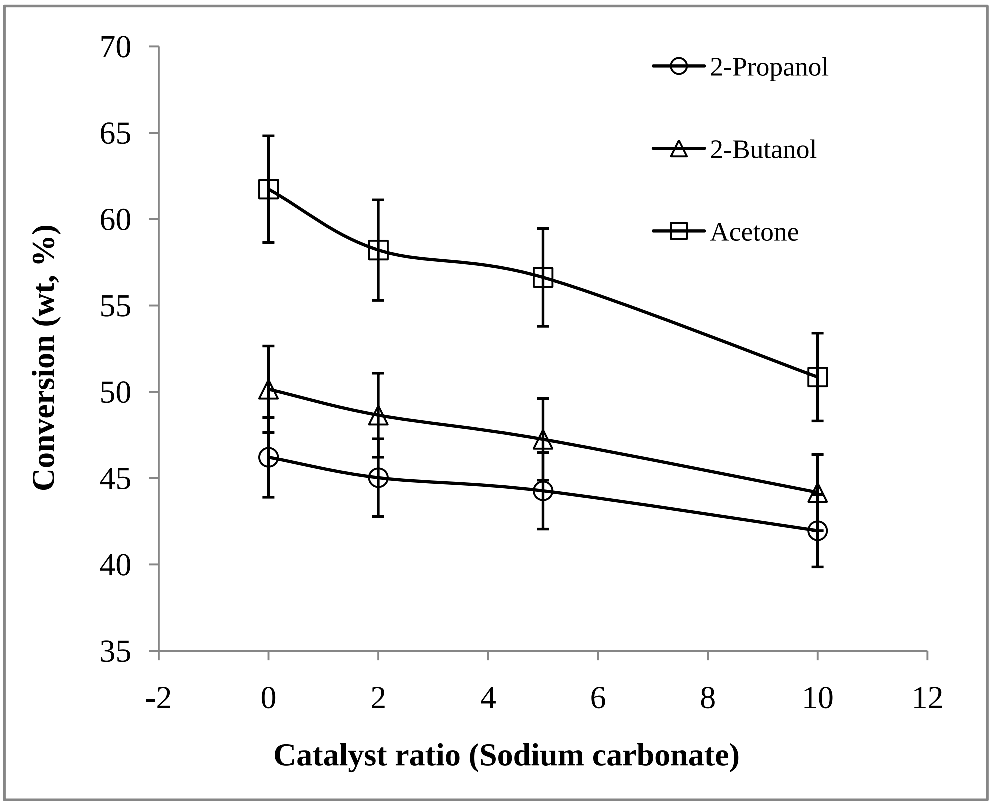
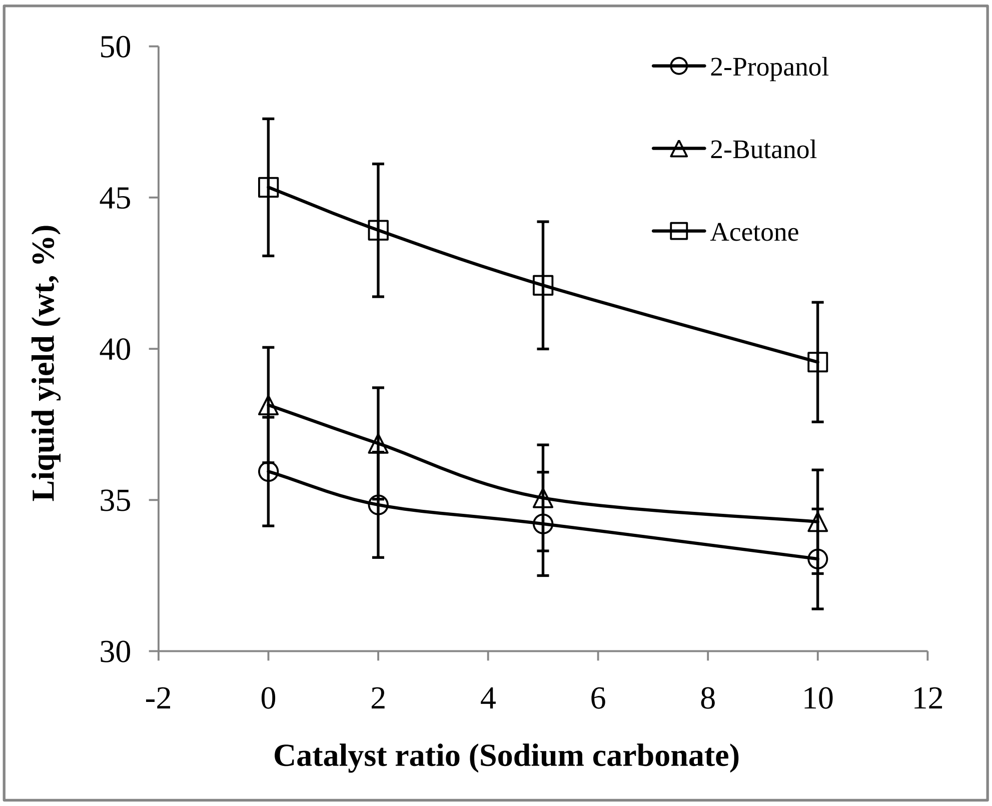


Figure 2 Effect of temperature on product yields


70
65
60
55
50
45
40
35
Conversion (wt, %)
-2
0
2
4
6
8
10
12
Catalyst ratio (Sodium hydroxide)
2-Propanol
2-Butanol
Acetone


50
45
40
35
30
Liquid yield (wt, %)
-2
0
2
4
6
8
10
12
Catalyst ratio (Sodium hydroxide)
2-Propanol
2-Butanol
Acetone


Conversion (wt, %)
70
65
60
55
50
45
40
35
-2
0
2
4
6
8
10
12
Catalyst ratio (Sodium carbonate)
2-Propanol
2-Butanol
Acetone


Liquid yield (wt, %)
50
45
40
35
30
-2
0
2
4
6
8
10
12
Catalyst ratio (Sodium carbonate)
2-Propanol
2-Butanol
Acetone

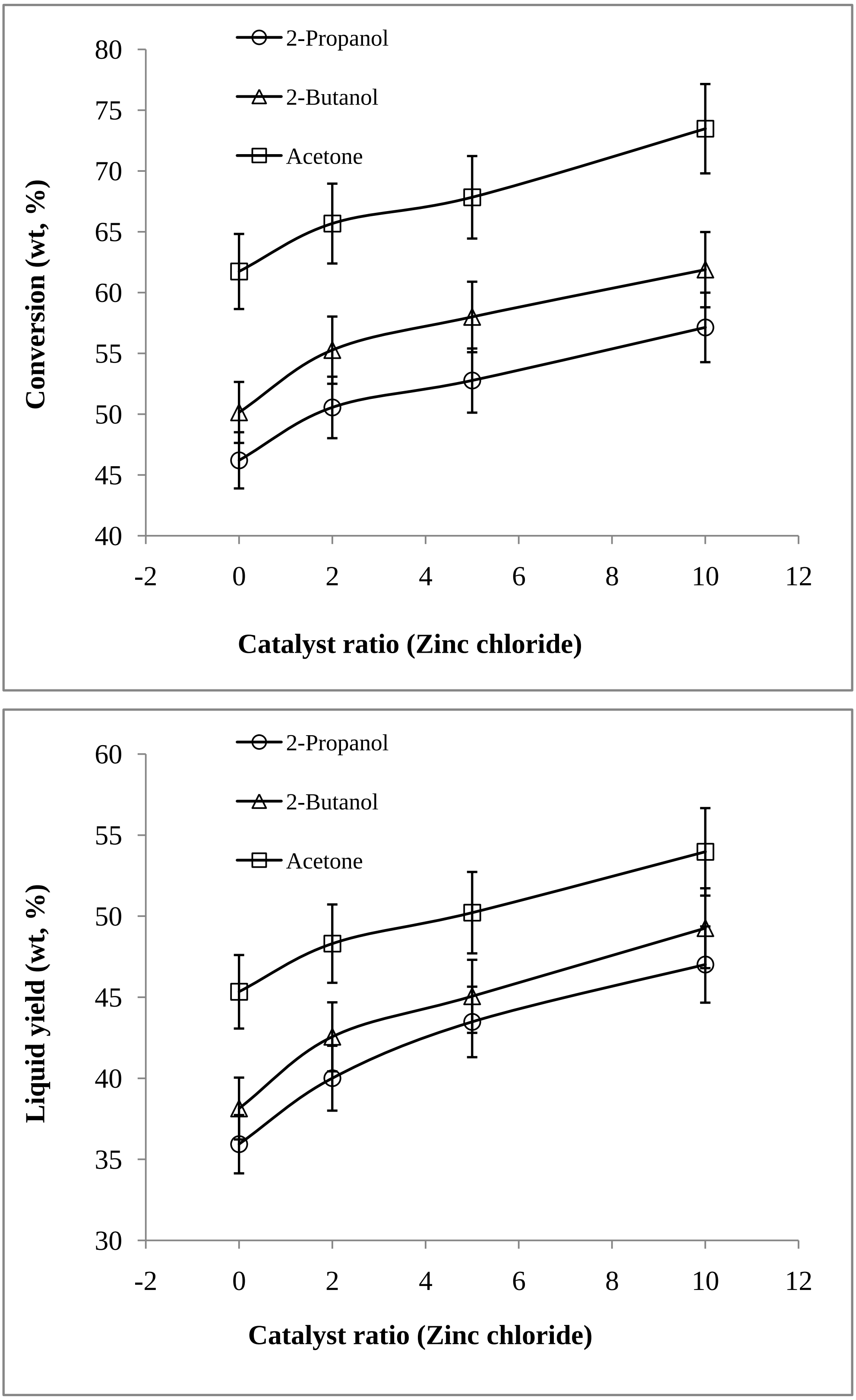
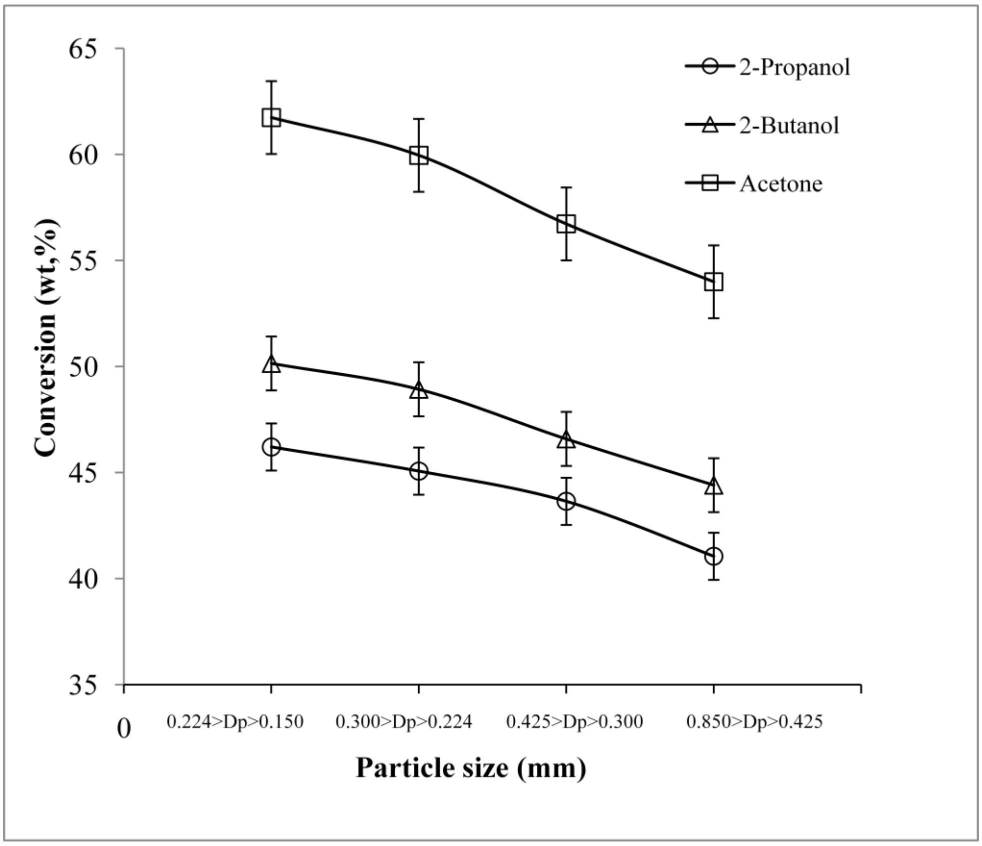


Figure 3 Effect of catalyst on conversion and liquid yields



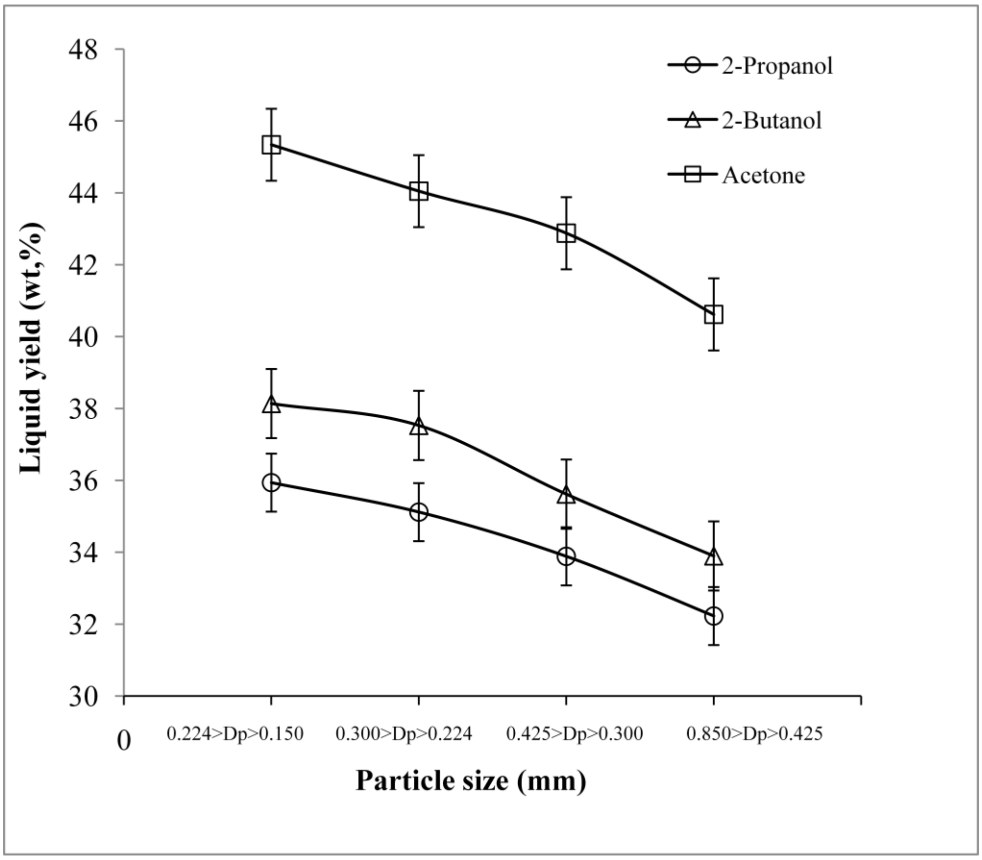
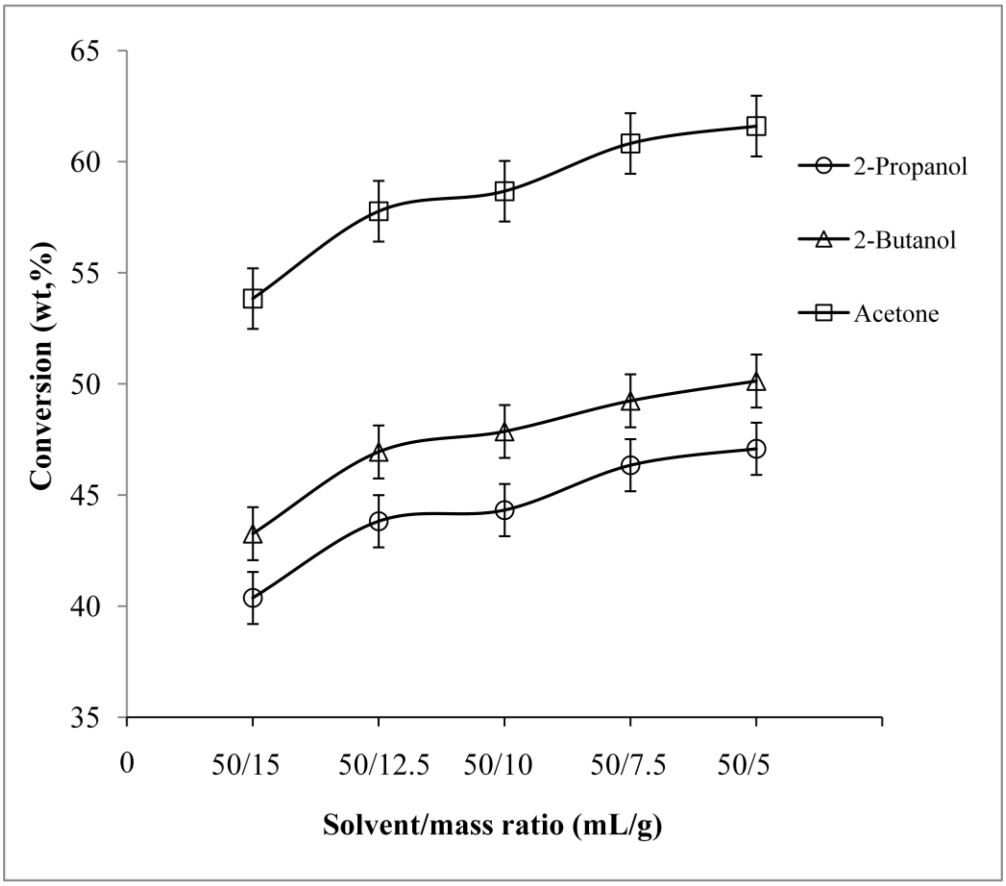


Figure 4 Effect of particle size on conversion and liquid yields



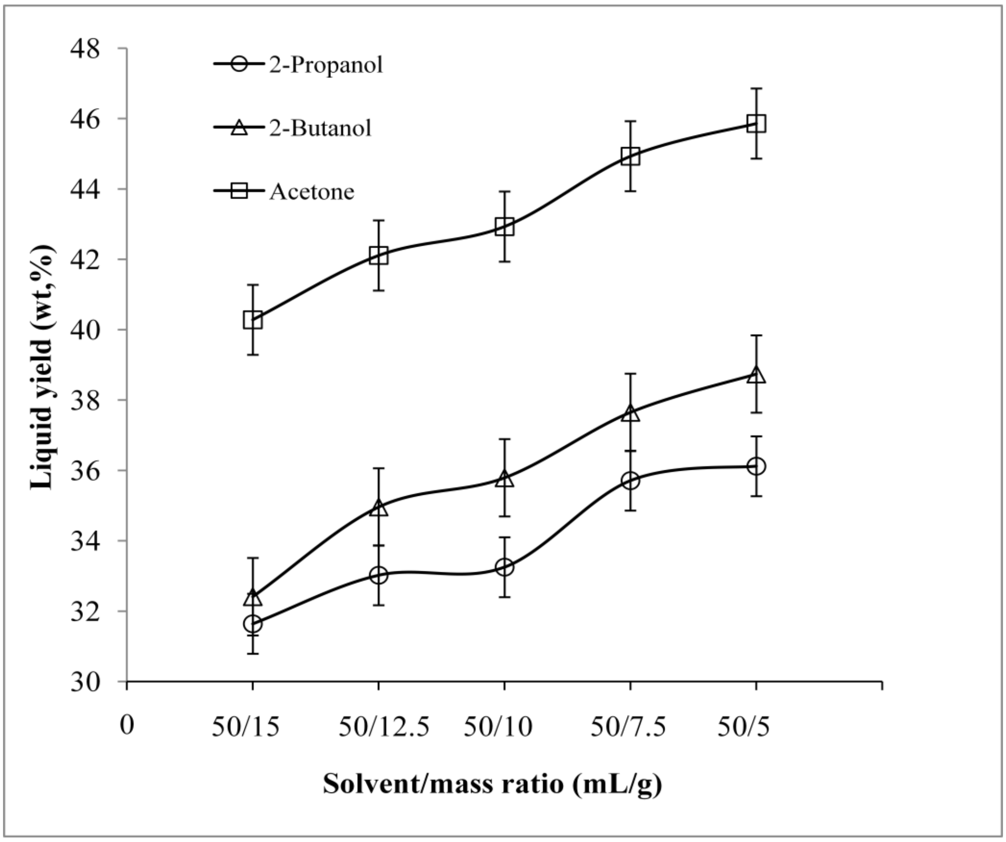


Figure 5 Effect of solvent/mass ratio on conversion and liquid yields

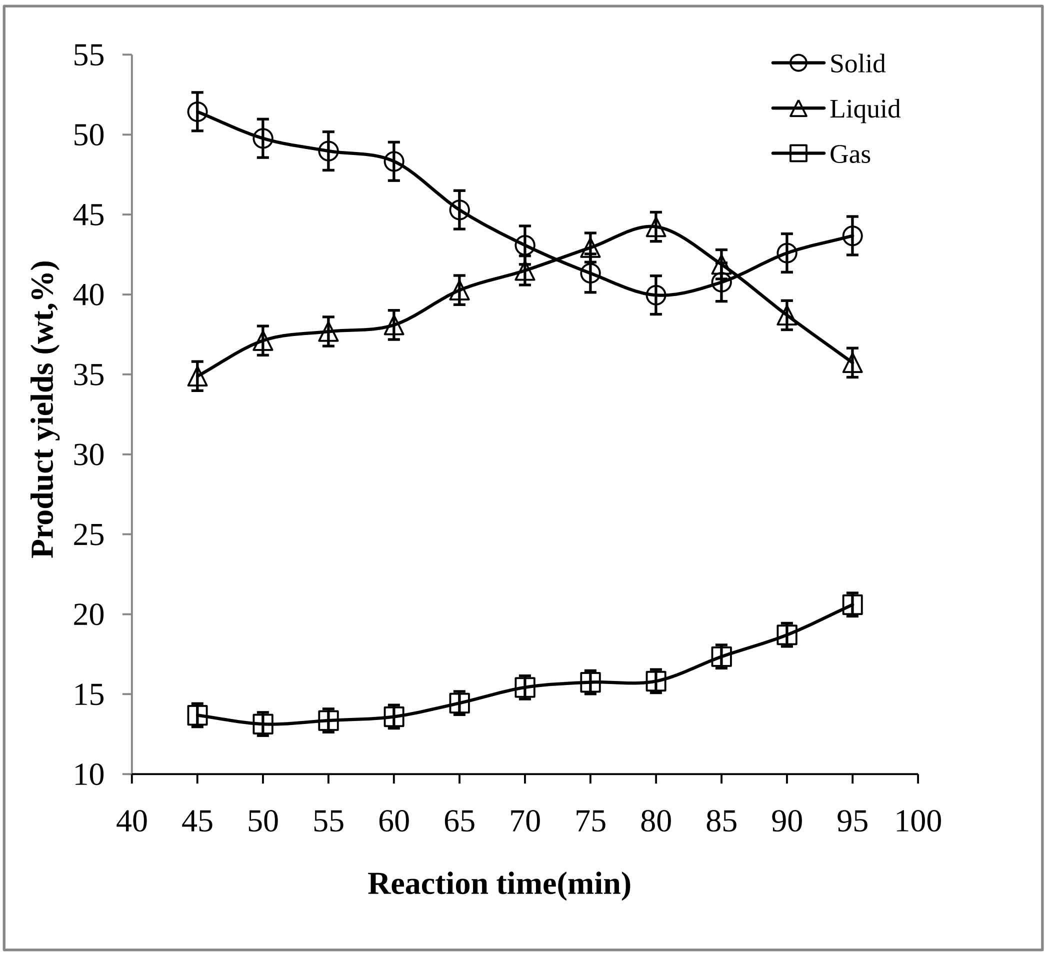


Figure 6 Effect of reaction time on product yields

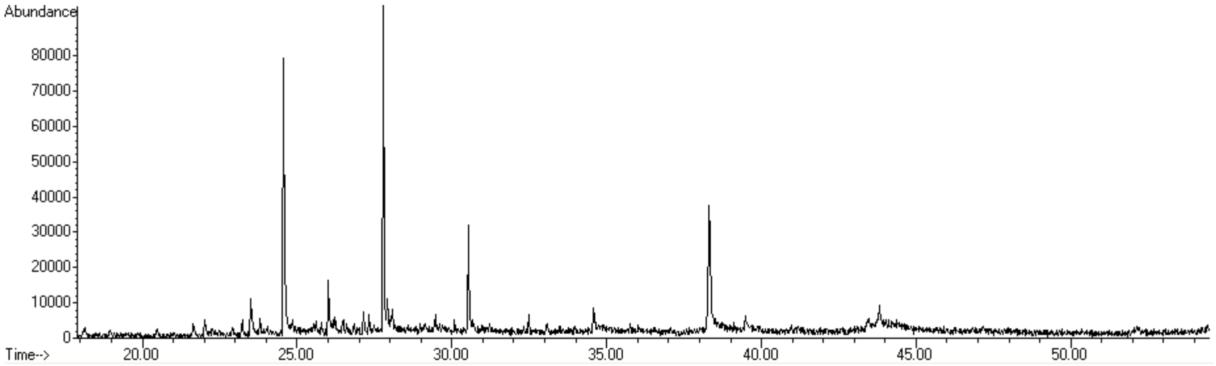


Figure 7 The total ion chromatogram of the liquid product obtained with 2-propanol as solvent and 10% Na_2CO_3 as catalyst at 300 ^oC

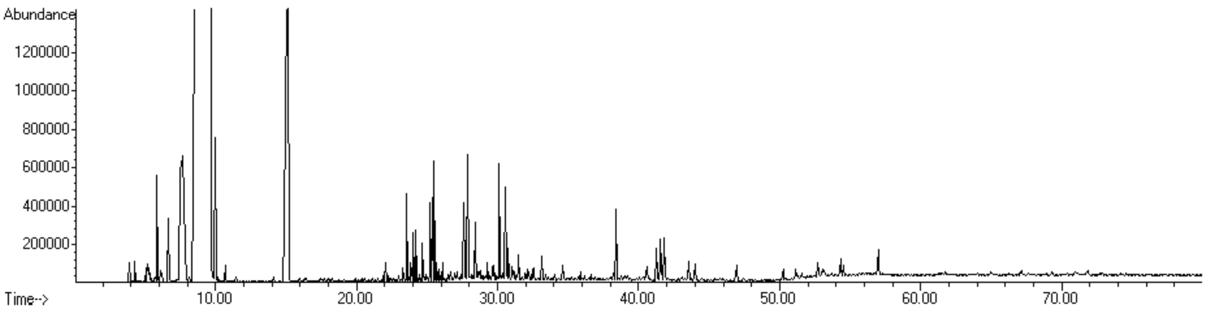


Figure 8 The total ion chromatogram of the liquid product obtained with 2-butanol as solvent and 10% NaOH as catalyst at 300 °C

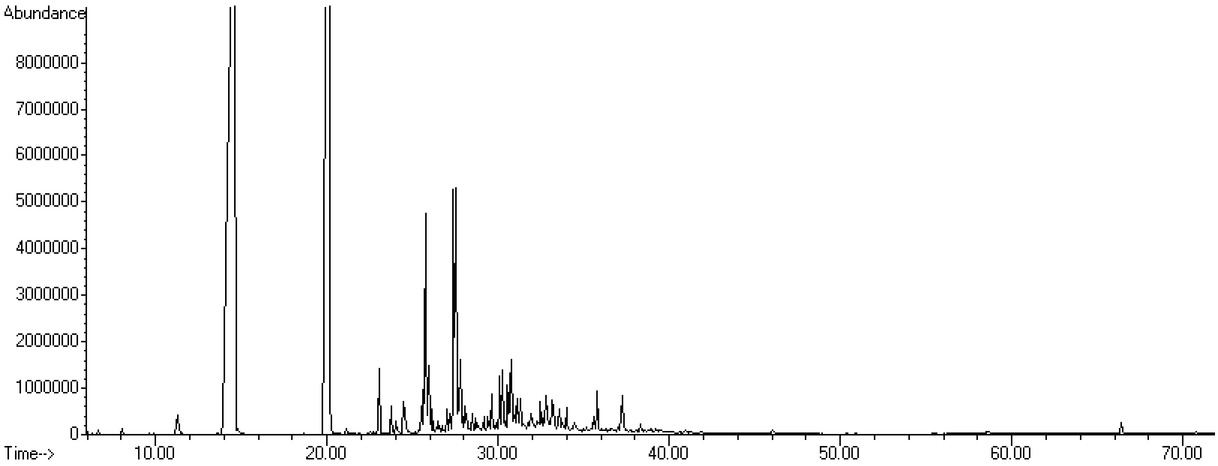


Figure 9 The total ion chromatogram of the liquid product obtained with acetone as solvent and 10% $ZnCl_2$ as catalyst at 300 °C

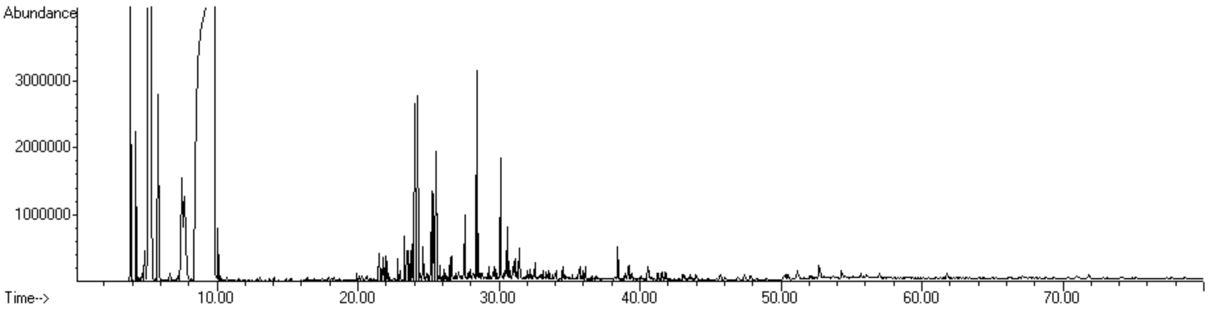


Figure 10 The total ion chromatogram of the liquid product obtained with 2-butanol as solvent and 10% $ZnCl_2$ as catalyst at 300 °C

19x4mm (300 x 300 DPI)

Optimization of process variables including temperature, solvent, catalyst, particle size, solvent/mass ratio and reaction time on supercritical liquefaction of giant fennel was conducted.