# Liquefaction of waste hazelnut shell by using sub- and supercritical solvents as a reaction medium

Emre Demirkaya, Orkan Dal, Aslı Yüksel*

Chemical Engineering Department, İzmir Institute of Technology, Urla, Izmir, 35430, Turkey

## HIGHLIGHTS

- Hazelnut shell was liquified in ethanol-acetone mixtures.
- Synergetic effect of the solvents provides higher bio-oil yield.
- Temperature, time, solvent ratios are important parameters for liquefaction.
- Different solvent ratios tend to different product distribution.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## ABSTRACT

Direct thermochemical biomass degradation to obtain bio-oil by using organic solvents is not a new process type, and it has some advantages over hydrothermal liquefaction technique. However, up to our best knowledge, in this study, hazelnut shell decomposition by using ethanol, acetone and their mixtures at sub/supercritical conditions was studied for the first time in literature. Experiments were carried out between 220–300 °C, at three different reaction times (30, 60 and 90 min) for five different solvent ratios. Highest solid conversion achieved at 300 °C by using pure ethanol was 64.2%, whereas highest bio-oil yield was found as 44.2% at 300 °C with 50/50 (EtOH/Ac: v/v). Ethanol and acetone showed different characteristics during the reactions and their effects on the conversion and bio-oil yield were discussed. Statistical analysis showed that time, temperature, ratio and synergy between temperature-time were affecting parameters for the conversion and bio-oil yield.

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## 1. Introduction

Interests on the alternative and renewable resources have been increasingly improved due to depletion of petroleum reserves, world's population growth, instabilities of markets and greenhouse gas emissions surplus [1–4]. As a renewable resource biomass rise above among other renewable resources because of its abundance and environmentally friendly effects [5]. It's a carbon neutral source, does not responsible for CO$_2$ concentration contribution to the atmosphere and helps recycling waste biomass [6]. For this reason, biomass utilization is significantly important to produce value-added chemicals, bio-oils or bio-fuels.

For a few decades, many efforts have been made to utilize lignocellulosic biomass better through thermochemical processes. Gasification [7], pyrolysis [8], direct combustion [9], liquefaction [10], and hydrothermal electrolysis [11] constitutes thermochemical processes. Bio-oil obtained from these processes mentioned above is not ready for direct use since all of the processes have some drawbacks. Among them, thermochemical liquefaction has lots of room for upgrading, and has caught significant attention since the process is environmentally friendly and can be carried out at low temperatures. There are some studies that were reported about

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**Table 1**
Thermodynamic properties of supercritical fluids [5].

| Solvent | $T_c$ (°C) | $P_c$ (MPa) | $\rho_c$ (g/cm$^3$) | Polarity[*] | Dielectric Constant[*] |
|---|---|---|---|---|---|
| Water | 374 | 22.06 | 0.3320 | 100 | 79.7 |
| Methanol | 240 | 8.09 | 0.2720 | 76.2 | 32.6 |
| Ethanol | 241 | 6.14 | 0.2760 | 65.4 | 22.4 |
| Acetone | 235 | 4.7 | 0.2779 | 35.5 | 20.6 |

[*] Polarities and dielectric constants are the ones at ambient pressure and temperature.

**Table 2**
Ultimate and structural analysis of hazelnut shell.

| Ultimate analysis (wt.%) | Hazelnut shell |
|---|---|
| Structural Analysis (%) | |
| Cellulose | 36.02 |
| Hemicellulose | 12.66 |
| Lignin | 40.14 |
| Extractives | 7.86 |
| Proximate Analysis (wt.%) | |
| Moisture | 8.93 |
| Ash | 1.48 |
| Protein | 3.11 |

lignocellulosic biomass conversion in sub/supercritical water, sub/supercritical ethanol and sub/supercritical acetone [12–15].

Supercritical fluids are neither gas nor liquid and they can have liquid-like and gas-like properties at the same time. Having a high density is a sign of liquid-like property, whereas low viscosity refers to the gas-like properties. Diffusivities are higher in supercritical fluids than in liquids but they are far lower than in gases. High density is responsible for high solving power of the liquid, while high diffusivity and low viscosity are in charge of controlling mass transfer rates of reactants. That leads to, diffusion limited reactions enhancement in sub/supercritical fluids with respect to liquids [16]. Some of the physical properties like dielectric constant, viscosity, and thermal conductivity are functions of density. It is also known that density depends on pressure, which means the physical properties of fluids in sub/supercritical region are highly temperature and pressure dependent. By changing temperature or pressure of a substance, it will allow the fluid to show different characteristics as a solvent, which is very important to be able to control [17].

Polar protic, dipolar aprotic and non-polar solvents can be used as a solvent for different purposes for any process according to desired polarity. Water and alcohols fall into the polar protic solvent category, which can donate hydrogen atom to an electronegative atom like oxygen. Acetone and acetonitrile are examples of dipolar aprotic solvent that have permanent dipole and cannot be able to donate hydrogen atom. Non-polar solvents, (e.g., hexane, benzene), on the other hand, are compounds that have very low dielectric constant even in ambient conditions and are not miscible with polar solvents. Some of the solvents properties that interest our study are given in Table 1 [5].

There are several investigations that were reported on thermochemical liquefaction of biomass using different solvents. Chan et al. (2014) were carried out hydrothermal liquefaction in sub and supercritical conditions of various biomasses (palm kernel shell, palm mesocarp fiber and empty frit brunch). They indicated that biomass content has significant effect on the product distribution [18]. Gozaydin and Yuksel (2017) conducted a study on valorization of hazelnut shell waste in hot compressed water and found that with the help of initial acid biomass conversion reached to 62% even at 280 °C [11]. Fan et al. (2011) investigated the effects of temperature and different solvents (acetone, ethanol, ethylene glycol, toluene and water) on the liquefaction of oil palm empty fruit brunch fibers, and the highest solid conversion and bio-oil yield was observed by using ethylene glycol, whereas water has slightly higher solid conversion and bio-oil yield than acetone and ethanol [13]. Huang et al. (2013) noticed that thermochemical liquefaction of rice husk in sub/supercritical ethanol gave almost no more increment on bio-oil yield after 280 °C, whereas gas product percentage was continuing to increase. The highest bio-oil yield observed was around 20% for catalyst free experiments [13]. Brand and Kim were researched the effect of individual lignocellulosic biomass constituents in supercritical ethanol and made a remarkable contribution to the literature. There are some missing points in literature to explain the behavior of sub/supercritical fluids, which will be mentioned in following parts, and their contribution fills one of these missing spots. Cellulose, hemicellulose (xylose) and lignin were investigated individually by using ethanol. Lignin conversion

was almost steady and not changing in the entire range of temperature they worked (between 290–350 °C), while almost all xylose conversion was finished at the temperature of 260 °C and cellulose conversion was still increasing at around 350 °C by showing around 95% conversion at that point [12].

Hazelnut is an agricultural crop that can be found in countries of Mediterranean Sea region. It grows mainly in Turkey, Spain, and Italy. However, Turkey is responsible for the highest amount of hazelnut production globally (ca. 75%) which corresponds to around 650,000 tons/yr. Hence, this high production amount comes with a price by causing large quantity of hazelnut shell as waste. These waste hazelnut shells are only used for heating or releasing to the nature [19]. Thus, by using thermochemical liquefaction processes utilization of waste hazelnut shells in the production of bio-oil or useful chemicals is probable.

Some of the recent studies showed that supercritical alcohols have some more benefits than subcritical water as a solvent in the direct liquefaction of biomass [19–23]. These benefits consist of better solubility of biomass and its intermediates, much easier product separation, having lower corrosivity, hydrogen donation ability and showing higher bio-crude/bio-oil yield [19]. The dominant mechanism in subcritical hydrothermal liquefaction includes hydrolytic and pyrolytic cleavage, whereas for supercritical ethanol-based liquefaction main degradation mechanism follows only pyrolytic cleavage. Thus, solid conversion, bio-oil yield and product distribution differs between subcritical water-based liquefaction and supercritical ethanol-based liquefaction [12]. Acetone, on the other hand, is a dipolar aprotic solvent and shows different polarity than ethanol. However, there is very limited work in literature about using acetone as a sub/supercritical fluid in biomass liquefaction [24].

Sub/supercritical water always attracted researchers more than sub/supercritical organic solvents, however as mentioned above, organic solvents have some advantages over water in sub/supercritical region. In order to gain better insight about the behavior of sub/supercritical organic solvents in biomass liquefaction, the major objective of this study is determined to investigate the effect two different organic solvents (ethanol and acetone) and their mixtures (EtOH/Ac - v/v 25/75, 50/50 and 75/25) at different temperatures (220, 260 and 300 °C) and reaction times (30, 60 and 90 min) for hazelnut shell liquefaction, in addition to characterizing the product distribution by FT-IR and GC–MS.

## 2. Materials and methods

### 2.1. Materials and chemicals

Hazelnut shell (HNS) was supplied from Ordu, Turkey. HNS was dried at 100 °C and was grinded to particle size of 600 μm. Ethanol (ACS grade) and acetone (ACS grade) were purchased from Merck. The structural analysis of hazelnut shell waste is given in Table 2.
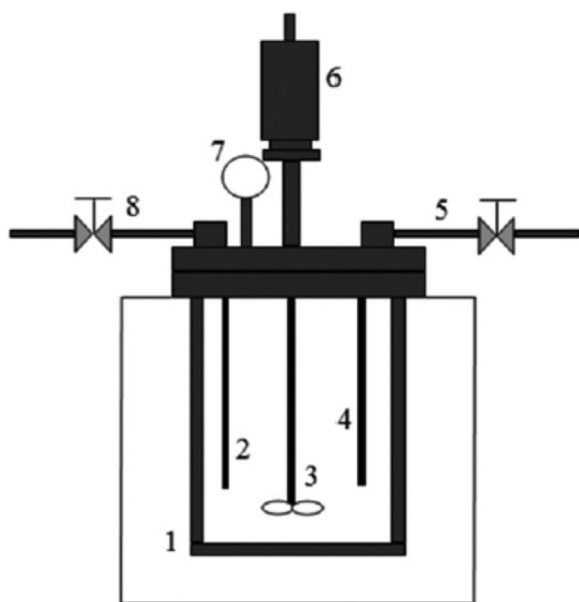
**Fig. 1.** Hydrothermal conversion reactor: (1) stainless steel vessel, (2) thermocouple, (3) stirring impeller, (4) gas inlet, (5) input nitrogen gas, (6) magnetically driven stirrer, (7) pressure gauge, (8) gas sample collector.

### 2.2. Liquefaction apparatus and procedure

The hydrothermal Liquefaction of hazelnut shell in reaction medium was carried out in a batch reactor (Parr 5500 Series, USA) made of SS-316 with a 300 mL of total volume equipped with magnetic stirrer as can be seen Fig. 1. In regular experiment, 4 g of waste hazelnut shell and solvents in different ratio was loaded to the vessel. After sealing, nitrogen was flowed through the reactor to remove air. Then, reactor was heated to desired temperature with the heating rate 7 °C/min. After reaction, reactor was cooled down to room temperature. Cooling rate was 6 °C/min. To separate liquid and solid part of the suspension was filtered through Whatman grade 307 filter paper under vacuum. Solid residue was dried at 80 °C in an oven overnight. Bio-oil and solvents were separated by using rotary evaporator under specific pressure and temperature according to nature of solvent.

The bio-oil yield, solid residue yield and solid conversion were calculated as using following equations:

$$Bio-oil\ yield\ (\%) = \frac{Mass\ of\ bio-oil}{Mass\ of\ initial\ hazelnut\ shell} x\ 100 \quad (1)$$

$$Solid\ conversion\ (\%) = \frac{Mass\ of\ initial\ hazelnut\ shell - Mass\ of\ solid\ residue}{Mass\ of\ initial\ hazelnut\ shell} x\ 100 \quad (2)$$

### 2.3. Analytical methods

#### 2.3.1. GC–MS Analysis analysis

Bio-oil samples were analyzed via gas chromatograph equipped with a mass spectrometer (GC–MS, Agilent 6890 N/5973 N Network, USA). The carrier gas was He at a flow rate of 1 mL/min. HP-5MS column, (0.25 mm × 30 m × 0.25 μm) was used. Oven temperature was started from 40 °C. After that, holding 3 min, followed by 12 °C/min heating rate to 190 °C and hold 1 min. With the heating rate of 8 °C/min temperature was increased 190 to 300 °C. and hold 20 min. The injected volume was 1 μL with 10:1 split ratio.

#### 2.3.2. FTIR analysis

Functional groups in bio-oil were examined in the wave number range of 4000- 650 cm$^{-1}$ by using Fourier Transform Infrared

**Table 3**
Change of biomass conversion and bio-oil yield with respect to time and solvent ratio at different temperatures a) 220 °C; b) 260 °C; c) 300 °C.

a)

| Solvent Ratio | Hazelnut Shell Conversion | | | Bio-Oil Yield | | |
|---|---|---|---|---|---|---|
| | 30 min | 60 min | 90 min | 30 min | 60 min | 90 min |
| 0:100 | 24.37 | 24.69 | 27.34 | 11.96 | 10.15 | 15.44 |
| 25:75 | 24.29 | 26.94 | 27.99 | 13.57 | 12.21 | 15.69 |
| 50:50 | 31.39 | 27.25 | 27.12 | 15.36 | 16.70 | 17.52 |
| 75:25 | 25.67 | 29.61 | 28.68 | 13.99 | 15.00 | 16.17 |
| 100:0 | 29.95 | 30.40 | 33.92 | 15.41 | 14.93 | 16.20 |

b)

| Solvent Ratio | Hazelnut Shell Conversion | | | Bio-Oil Yield | | |
|---|---|---|---|---|---|---|
| | 30 min | 60 min | 90 min | 30 min | 60 min | 90 min |
| 0:100 | 34.77 | 40.01 | 41.02 | 16.68 | 18.55 | 18.38 |
| 25:75 | 34.94 | 41.72 | 43.24 | 17.84 | 19.35 | 21.20 |
| 50:50 | 34.45 | 39.65 | 41.90 | 19.64 | 20.50 | 24.03 |
| 75:25 | 36.84 | 42.66 | 42.89 | 18.35 | 18.73 | 17.39 |
| 100:0 | 40.90 | 42.13 | 42.94 | 15.07 | 15.42 | 15.70 |

c)

| Solvent Ratio | Hazelnut Shell Conversion | | | Bio-Oil Yield | | |
|---|---|---|---|---|---|---|
| | 30 min | 60 min | 90 min | 30 min | 60 min | 90 min |
| 0:100 | 52.04 | 54.26 | 55.90 | 30.33 | 29.72 | 37.88 |
| 25:75 | 54.19 | 56.72 | 58.24 | 31.60 | 29.88 | 39.41 |
| 50:50 | 57.43 | 58.58 | 62.48 | 34.36 | 36.65 | 44.23 |
| 75:25 | 54.21 | 60.31 | 61.81 | 28.49 | 34.77 | 36.55 |
| 100:0 | 57.62 | 62.94 | 64.28 | 30.62 | 31.24 | 31.60 |

Spectrometry that equipped with attenuated total reflectance (ATR-FTIR) (Perkin Elmer-Spectra Two, USA).

## 3. Results and discussion

### 3.1. Effect of temperature

To investigate the effect of temperature on the conversion of waste hazelnut shell and bio-oil yield, experiments were carried out with varying temperatures such as 220 °C, 260 °C and 300 °C. The results obtained from the thermochemical liquefaction of waste hazelnut shell, including conversion and bio-oil yield are given in Table 3.

As it can be seen in Fig. 2 and Fig. 3, for the whole range of investigated temperatures, the conversion of waste hazelnut shell increased with increasing reaction temperature with respect to each solvent ratio (except 50/50 mixture of EtOH/Ac - v/v) and reaction time. It is clear from Table 3 that, the highest hazelnut shell conversion (64%) was achieved at 300 °C by using pure ethanol as solvent (100/0 – v/v) for 90 min reaction time. On the other hand, the lowest conversion was recorded as 24% that was at 220 °C by using pure acetone as solvent (0/100 – v/v) for 30 min reaction time.

Hazelnut shell like other biomasses consists of cellulose, hemicellulose and lignin structures and the structural analysis results, which was given in Table 2, show that cellulose, hemicellulose and lignin content of the hazelnut shell are 35.72%, 12.86% and 39.54%, respectively. Individual biomass constituents' behavior in sub/supercritical fluids gives us better insight about what is going on here. According to Brand and Kim, almost all of the hemicellulose is reached complete conversion at 265 °C, and cellulose has only 11.6% conversion at that temperature [12]. Therefore, it can be said that, at 220 °C nearly the whole degradation of hazelnut shell occurs mainly by hemicellulose and by little amount of cellulose. Because, when compared to cellulose and lignin, decomposition of hemicellulose at lower temperatures is easier due to its amorphous
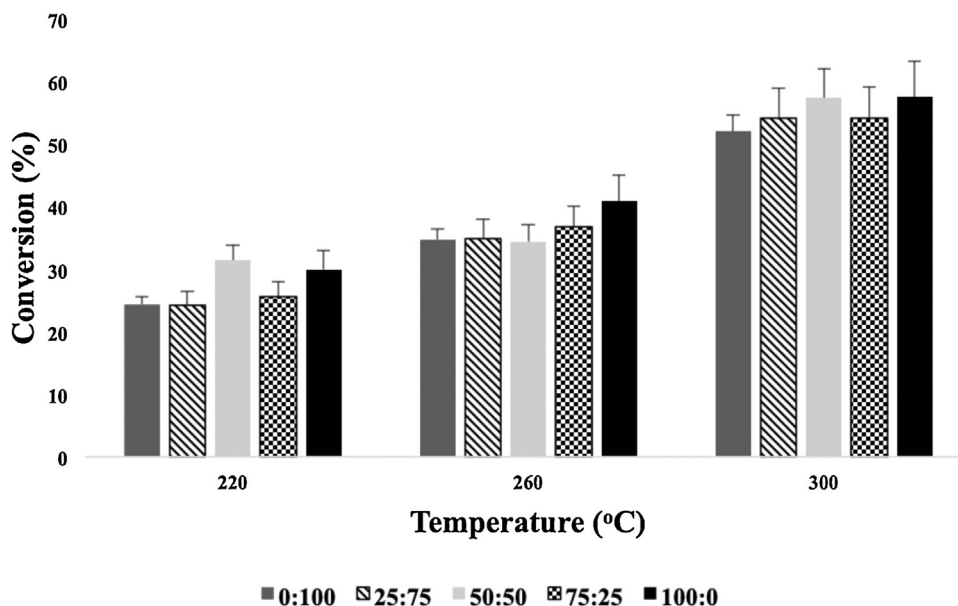
**Fig. 2.** Temperature and solvent effects for hazelnut shell conversion for 30 min reaction time.

structure [5]. On the other hand, bio-oil yield at 220 °C is averagely around 14%, which is very low as expected.

Since the critical temperature and pressures of pure acetone and ethanol are 235 °C & 4.8 MPa and 243 °C & 6.39 MPa [5], experiments conducted at 220 °C belong to the subcritical region of both solvents, whereas, experiments carried out at 260 °C and 300 °C correspond to the supercritical region of both solvents. Therefore, it is plausible to think that, by passing into the supercritical region hazelnut shell conversion and bio-oil yield must be increased. The main reasons behind that are high diffusivity rates, low dielectric constant values and changing polarization in supercritical region [25,26]. The results obtained from the supercritical ethanol liquefaction of hazelnut shell indicates that, by increasing temperature from 220 °C to 260 °C the average biomass conversion was increased from ca. 27% to 40%, while bio-oil yield was slightly increased from 14.7% to 18.5%. Conversion values seem to be consistent with the hypothesis, but there is a slight increment in bio-oil yield. However, this trend is still reasonable, because, as mentioned Brand and Kim, feedstock cellulose gives only around 5% of bio-oil at 265 °C, while lignin has no data below 290 °C. Moreover, it's known that cellulose and lignin thermogravimetric analysis show similar weight loss until 350 °C, and decomposition of lignin is harder than cellulose [12]. For this reason, it is possible to say that very similar amount of bio-oil yield comes from lignin. These explains why there is a slight increment on bio-oil yield with respect to 220 °C (Figs. 2 and 3).

By increasing the temperature from 260 °C to 300 °C, resulted with the increment of average hazelnut conversion from 40% to 58.1%, and almost doubling of bio-oil yield from 18.5% to 33.8%. Even if it's known biomass conversion and bio-oil yield strongly depends on biomass type and solvent type, the results obtained in this work consistent with some of the works in literature [5,10,19]. Both cellulose and lignin above 250 °C decomposes by depolymerization reactions [12]. According to Table 3, it's not surprising there is a huge increment in bio-oil yield between 260 °C and 300 °C.

### 3.2. Effect of solvent type

The experimental results of sub/supercritical ethanol and sub/supercritical acetone and their mixtures are given for solid conversion in Fig. 2 and Fig. 3. Under same conditions, obtained bio-oil yields are given in Figs. 4 and 5 Different solvent ratios (EtOH/Ac - v/v): 0/100, 25/75, 50/50, 75/25, 100/0) were investigated for the solid conversion and bio-oil yield obtained from waste hazelnut shell. At the temperature of 220 °C, bio-oil yield for pure ethanol was found slightly higher than pure acetone, whereas for biomass conversion ethanol gave higher conversion of hazelnut shell at any reaction temperature. This is probable because while approaching to near critical conditions, the density and dielectric constant decreases which leads to reducing interaction between hazelnut shell particles and solvent [25,26]. As a result, liquid products yield will be less than the supercritical region. Since pure acetone has lower critical temperature (235 °C) than pure ethanol (241 °C), encountering with this behavior at 220 °C is likely.

Based on the results presented in Figs. 4 and 5, by increasing temperature from 220 °C to 260 °C, the experiments conducted with pure acetone reached the same value of bio-oil yield with pure ethanol processes. As previously mentioned in Part 3.1, conversion increases by increasing temperature. When temperature is increased at some point it will be sufficiently high to break the solid biomass bonds and depolymerization occurs [27]. In solvents' aspect, when high temperature and pressure were applied on a polar protic solvent, which includes hydrogen bonding (pure ethanol), the hydrogen bonds in the cellulose and hemicellulose start to break down. Because of the glycosidic bonds of hemicellulose and cellulose are polar, and by the help of a polar protic solvent in sub/supercritical region they depolymerize very fast. Also, since ethanol has a big advantage which is hydrogen-bond donating, presence of ethanol as a solvent in thermochemical liquefaction processes stabilize the free radicals and help to obtain higher biomass conversion [28]. Acetone, on the other hand, is a dipolar aprotic solvent and does not includes hydrogen bond to stabilize the reaction medium which leads to slightly lower biomass conversion compared with ethanol.

As it was mentioned in previous part, highest conversion and bio-oil yield of hazelnut shell was observed at 300 °C. Ethanol shows higher solid conversion during all reaction times (30 min, 60 min, 90 min) compared to acetone and their mixtures. The reason behind that is the same as explained in the case of 260 °C. Nevertheless, by examining the bio-oil yield it can be seen that the highest bio-oil yield (44.2%) was obtained with equal amount of solvent mixture (EtOH/Ac - v/v: 50:50) as seen in Fig. 5. Also,
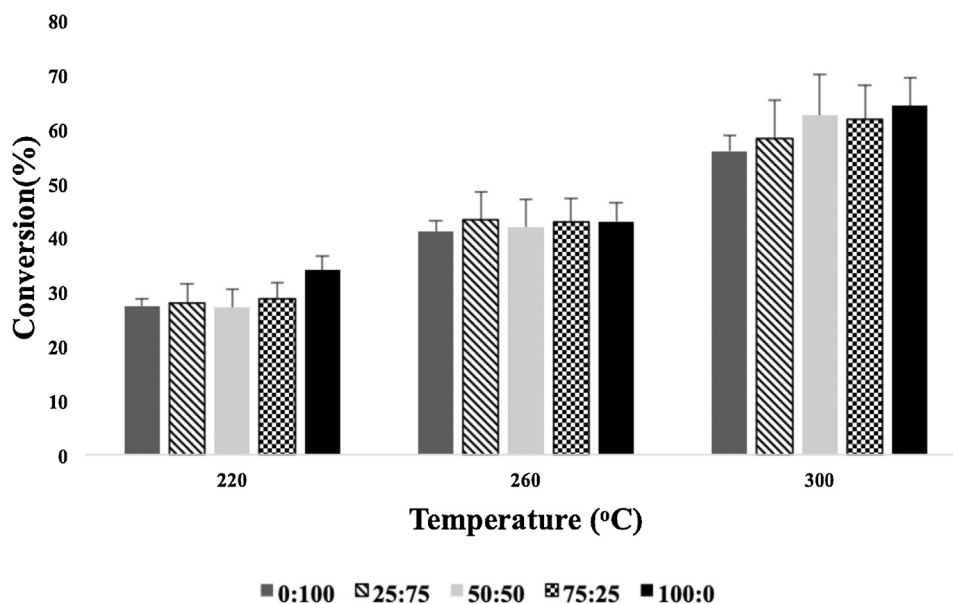
**Fig. 3.** Temperature and solvent effects for hazelnut shell conversion for 90 min reaction time.
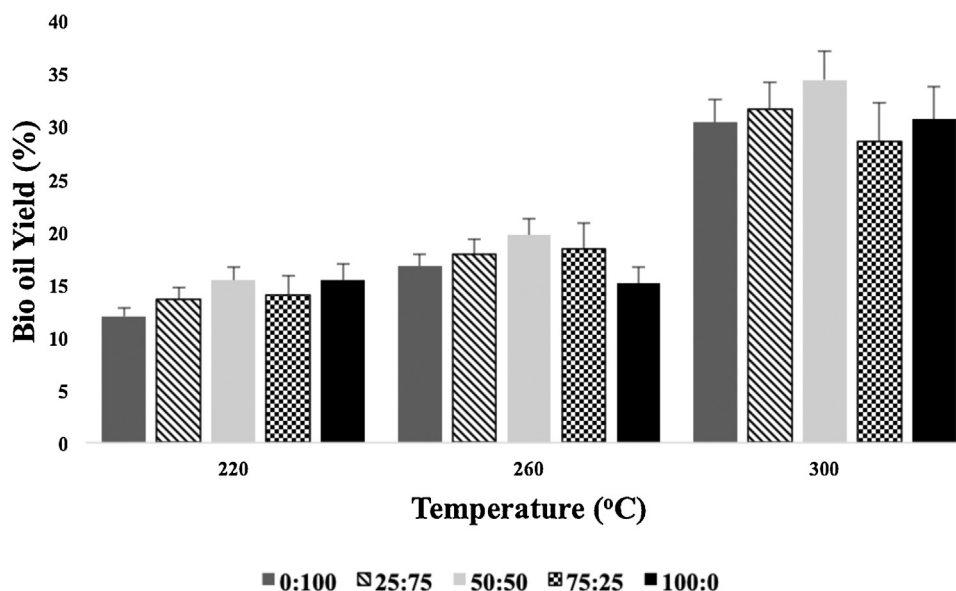


**Fig. 4.** Temperature and solvent effects for bio-oil yield for 30 min reaction time.

it is apparent that bio-oil yield of the experiments conducted with pure acetone was higher (max 37.88%) than that was obtained with pure ethanol (max 31.6%). This might be explained with two characteristics of acetone: it is an aprotic solvent (no hydrogen bond donation) and less polar than ethanol [5]. Polarity of the acetone is almost half of the ethanol, even if they have very similar critical temperature, density and dielectric constant values. That's the reason why ethanol is more efficient to solve polar compounds, whereas acetone is more efficient for less polar compounds. Moreover, acetone is not a hydrogen donor solvent and does not show a stabilization effect as a solvent. If we combine them all, it is reasonable to have higher bio-oil yield in pure acetone processes than that was obtained with pure ethanol at 300 °C.

### 3.3. Effect of time

Degradation of hazelnut shell showed slight increments with increasing time for both biomass conversion and bio-oil yield for each temperature and solvent ratio as indicated in Table 3. For experiments conducted at 220 °C, results showed similar behavior. Increasing time leads to slight increment of conversion and bio-oil yield within the error percentage for each solvent except 50/50 (v/v) mixture of acetone and ethanol for conversion. It shows opposite behavior compared to other solvents. Its value decreases from 31.4% (30 min) to 27.12% (90 min). This might be explained with the formation of some intermediate products at 30th min, which may be repolymerized onto the solids at 90th min.

By comparing the reaction time effect for each solvent for the experiments carried out at 300 °C, it is possible to say that there is a slight increment in hazelnut shell conversion from 30 min to 90 min. Increasing the reaction time between 30 min and 60 min does not affect bio-oil yield that much as seen on Table 3 (c). However, when the operation time is increased to 90 min, except pure ethanol, there is more than 20% increment for bio-oil yield with respect to the experiments carried out at 260 °C. The highest bio-oil yield was observed for 50/50 (v/v) mixture as 44.2%.
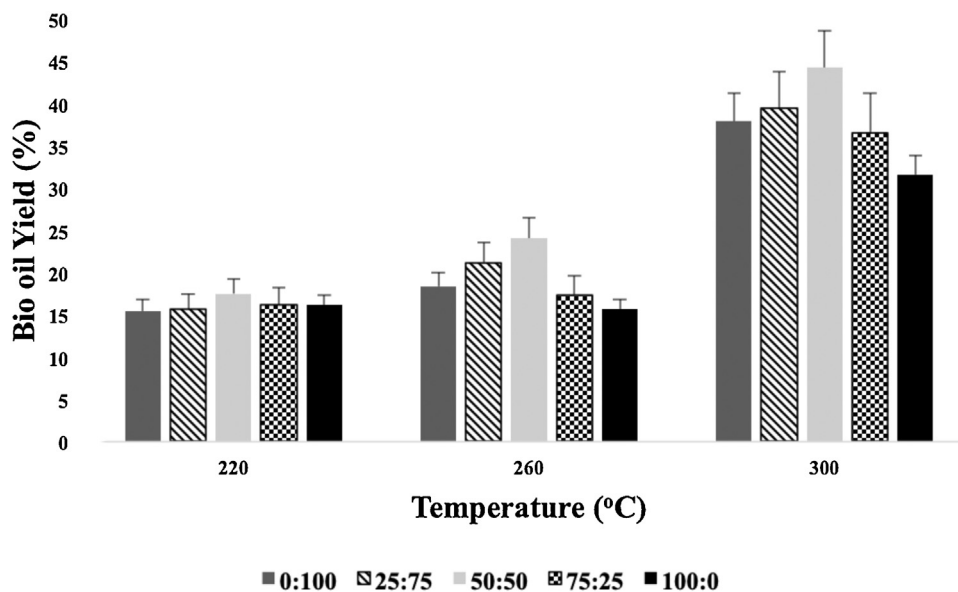
**Fig. 5.** Temperature and solvent effect for bio-oil yield for 90 min reaction time.
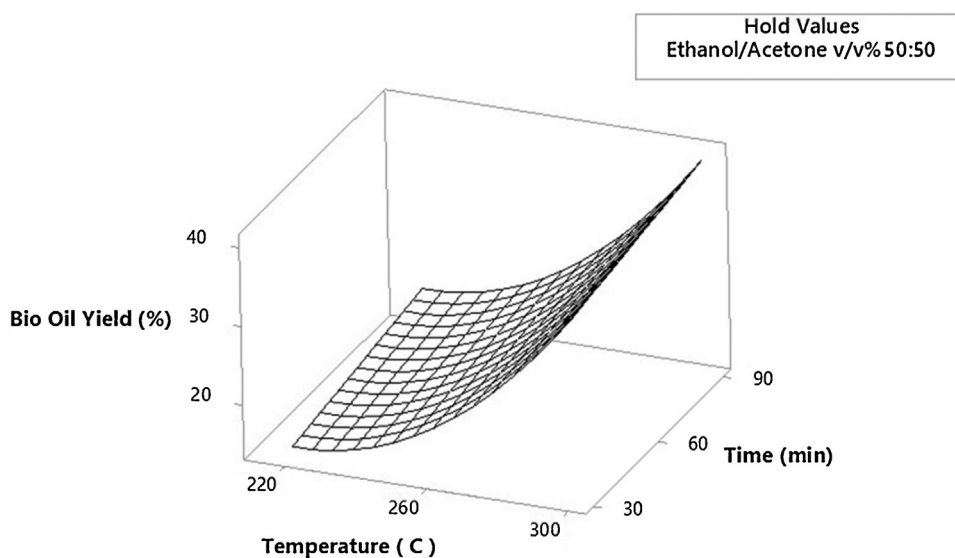


**Fig. 6.** Response surface plot of bio-oil yield from hazelnut shell waste.

### 3.4. Analysis of variance (ANOVA)

Statistical analysis of time, temperature and ethanol/acetone ratio (v/v) was investigated on biomass conversion and bio-oil yield to evaluate the significance of results by ANOVA via using MINITAB 17 software. Significance level was accepted as 95% ($p \leq 0.05$) Histograms and residual plots show the linear distributed data (Figure S1 and S2), which confirms the model accuracy.

ANOVA results of hazelnut shell conversion and bio-oil yield were given as Table S1 and S2. While all individual parameters (temperature, time and ethanol/acetone ratio - v/v) affected the conversion and bio oil yield ($p \leq 0.05$), some 2-way interactions, such as temperature-ratio and time-ratio, were not significant on conversion and bio-oil yield since their p-values were greater than 0.05. Table S2 describes reduced model of hazelnut shell conversion and bio-oil yield. After reduction of model p-values of all model terms were smaller than 0.05.

Response surface plots for conversion and bio-oil yield were shown in Figs. 6 and 7. Temperature and time had positive effect on hazelnut conversion and bio-oil yield. At 90 min with 50:50 ethanol/acetone (v/v) ratio, conversion was increased from 25.78 to 62.48%, whereas bio oil yield was increased from 17.52 to 44.23% under same conditions.

The optimization results for hazelnut conversion and bio-oil yield were given in Fig. 8. Conversion and bio oil yield were maximized. According to response optimization, optimum results for maximum conversion and maximum bio-oil yield were found at 300 °C, 90 min and with 50:50 ethanol/acetone (v/v) ratio as 59.86 and 40.12%, respectively.

### 3.5. GC–MS Analysis analysis

The major chemical compounds formed in bio-oil products at 300 °C by using sub/supercritical ethanol, acetone and their mixtures (EtOH/Ac v/v): 25/75, 50/50 & 75/25 were characterized by GC—MS analysis and presented in Table 4. As it can be seen from the table, according to their chemical functional groups 5 different major groups (e.g. acids, aldehydes & ketones, cyclic compounds,
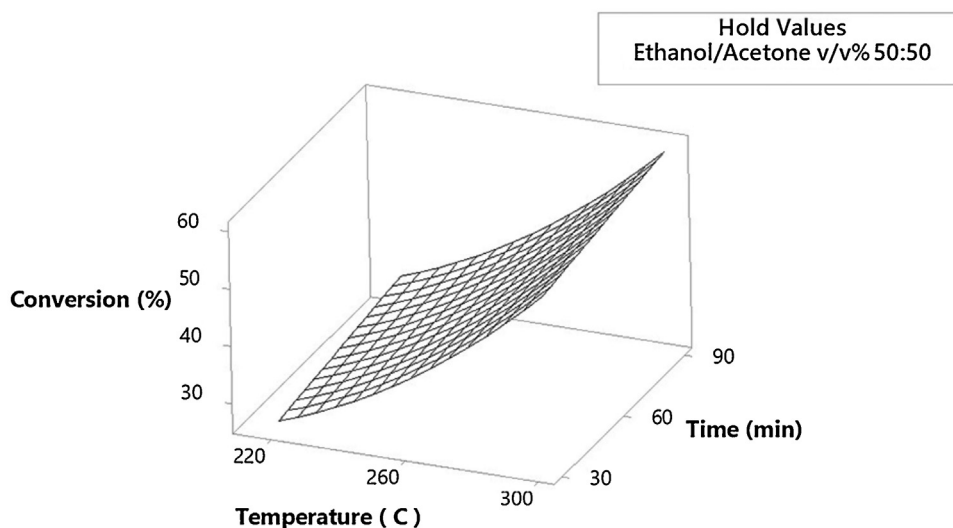
Fig. 7. Response surface plot for the conversion of hazelnut shell waste.

**Table 4**
GC–MS results for major compounds of hazelnut shell liquefaction in ethanol, acetone and their mixtures at 300 °C.

| Peak no | Retention time (min) | Solvent ratio (EtOH:Ac -v:v) | | | | | Compound |
|---------|----------------------|--------|-------|-------|-------|-------|----------|
| | | 0:100 | 25:75 | 50:50 | 75:25 | 100:0 | |
| 1 | 4.553 | 3.28 | 2.91 | 3.91 | 2.03 | – | 2,5-Hexanedione |
| 2 | 5.206 | 2.41 | 1.14 | 1.01 | 0.73 | – | 2-Cyclopenten-1-one, 3-methyl- |
| 3 | 5.639 | 1.11 | 1.45 | 2.04 | 1.40 | – | L-borneol |
| 4 | 6.16 | 2.22 | 1.85 | 2.35 | 0.11 | – | 3,6-Heptanedione |
| 5 | 6.374 | 3.05 | 2.24 | 3.00 | 1.86 | – | Butanoic acid, 4-hydroxy-2-methylene- |
| 6 | 6.984 | 2.32 | 3.94 | 5.23 | 4.03 | 6.02 | Propanoic acid, 2-methyl-, anhydride |
| 7 | 7.168 | 4.01 | 3.11 | 0.44 | 3.23 | 4.74 | Phenol, 2-methoxy- |
| 8 | 7.364 | 1.28 | 4.41 | 4.28 | 2.91 | – | 2-Cyclohexen-1-one, 3,5-dimethyl- |
| 9 | 7.447 | 2.56 | 0.94 | – | – | – | 2,5-Heptadien-4-one, 2,6-dimethyl- |
| 10 | 9.694 | 5.81 | 3.73 | 4.57 | 3.98 | 3.74 | Phenol, 4-ethyl-2-methoxy- |
| 11 | 10.328 | 2.67 | 1.20 | 0.72 | 0.32 | – | Cyclohexanone, 2-(hydroxymethylene)-3-methyl-6-(1-methylethyl)- |
| 12 | 10.553 | 1.72 | 1.77 | 0.96 | 2.10 | 2.76 | Phenol, 2,6-dimethoxy- |
| 13 | 10.621 | 1.36 | 0.69 | 2.22 | 0.71 | – | Phenol, 2-methoxy-5-(1-propenyl)-, (E)- |
| 14 | 10.725 | 2.91 | 1.64 | 0.54 | 1.81 | 2.57 | Phenol, 2-methoxy-4-propyl- |
| 15 | 10.986 | – | – | 2.17 | 1.79 | 2.25 | Ethyl beta-d-riboside |
| 16 | 11.188 | 2.98 | 0.84 | 0.98 | 0.83 | – | 2,5-Cyclohexadiene-1,4-dione, 2-methyl-5-(1-methylethyl)- |
| 17 | 17.057 | 2.87 | 0.78 | 0.76 | – | – | n-Hexadecanoic acid |
| 18 | 17.399 | – | 2.42 | 0.18 | 3.22 | 4.51 | Hexadecanoic acid, ethyl ester |
| 19 | 18.640 | 3.08 | 2.03 | 2.93 | 1.08 | 0.55 | 10-Octadecenoic acid, methyl ester |
| 20 | 19.186 | 18.19 | 6.25 | 1.39 | 1.48 | 0.39 | Oleic acid |
| 21 | 19.335 | – | 3.68 | 2.93 | 4.92 | 6.76 | 9,12-Octadecadienoic acid, ethyl ester |
| 22 | 19.429 | – | 18.25 | 22.90 | 27.79 | 34.63 | Ethyl Oleate |
| 23 | 19.665 | – | 1.48 | 1.34 | 1.66 | 1.87 | Octadecanoic acid, ethyl ester |

esters and phenolic compounds) constitute lots of chemical compounds. Hazelnut shell liquefaction in supercritical ethanol, and its mixtures with acetone showed that ethyl oleate was the major compound found in each bio-oil product. In supercritical ethanol liquefaction of hazelnut shell, second and third major peaks were belonging to ethyl esters, which were 9, 12-octadecadienoic acid ethyl ester and hexadecanoic acid ethyl ester, respectively. On the other hand, acetone had the highest amount of oleic acid with respect to GC—MS analysis results. Second and third major peaks of supercritical acetone liquefaction of hazelnut shell were found as 4-ethyl-2-methoxy phenol and 2-methoxy phenol, respectively.

Phenol is mainly generated by the degradation of low molecular weight lignin [29]. The lowest total phenolic content yield can be seen in the bio-oil products of 50/50 (v/v) mixture of ethanol and acetone. Previous studies mentioned that having no phenolic compound in the oil product is a sign of delignification operation [30,31]. However, aromatic compounds are also mainly degraded

from lignin [32]. Since low amount of phenolic compounds still exist in bio-oil product, total delignification cannot be mentioned, but it can be said that, 50/50 (v/v) mixture of ethanol and acetone is a better delignifying solvent mixture than pure solvents and different mixture ratios.

Some acids are found in bio-oil product, which are known as coming from decomposition of hemicellulose and cellulose. As an acid, mainly butanoic acid, butanedioic acid, tetradecanoic acid, propanoic acid, n-hexadecanoic acid and oleic acid themselves or derivatives were detected in GC–MS analysis.

### 3.6. FT-IR analysis

The functional groups of hazelnut shell were investigated by FTIR-ATR and the results were shown in Figs. 9 and 10. According to the literature [33,34], peaks around 3316 cm$^{-1}$ corresponds to the vibration of −OH groups. The peak of −OH band is broad because of
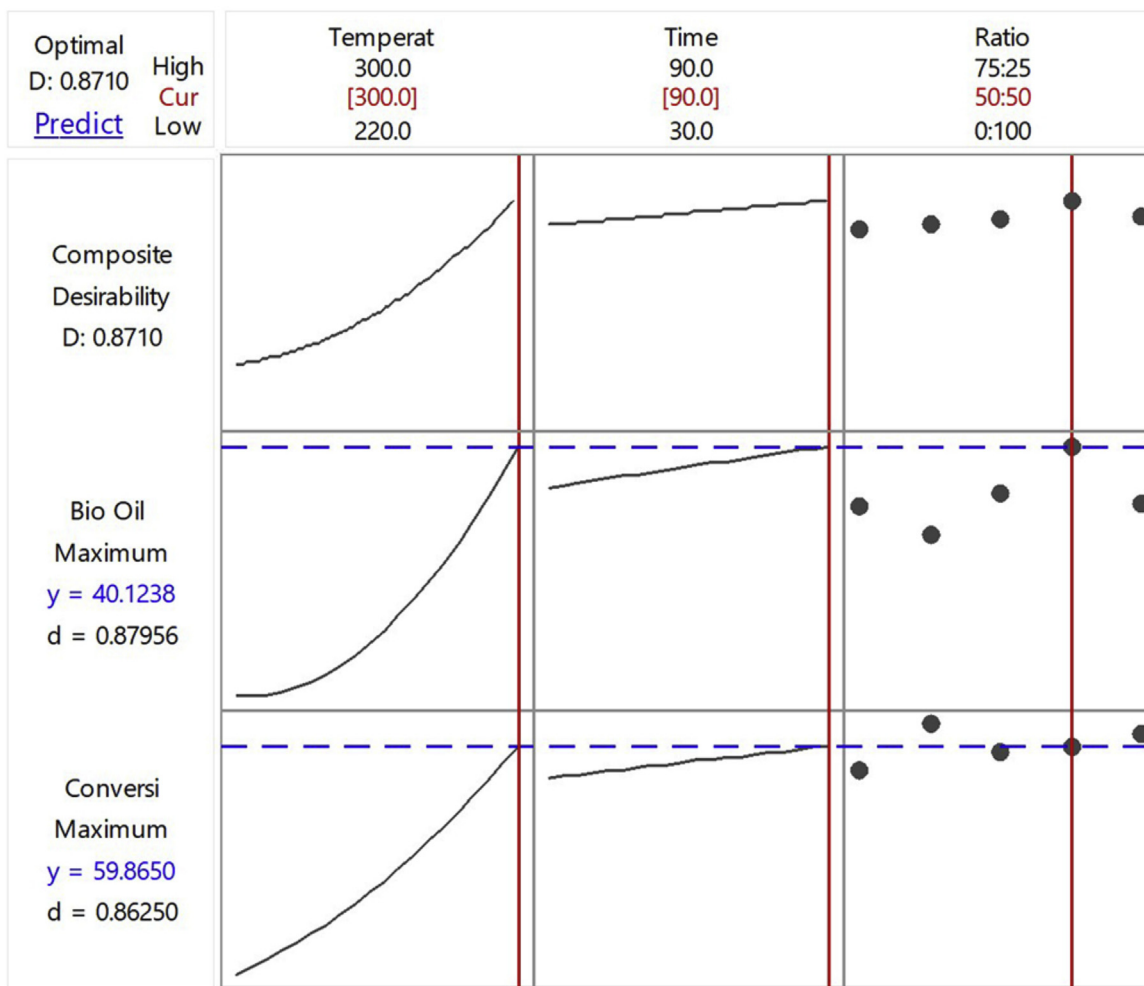
**Fig. 8.** Optimum operating conversion for maximum conversion and maximum bio-oil yield.
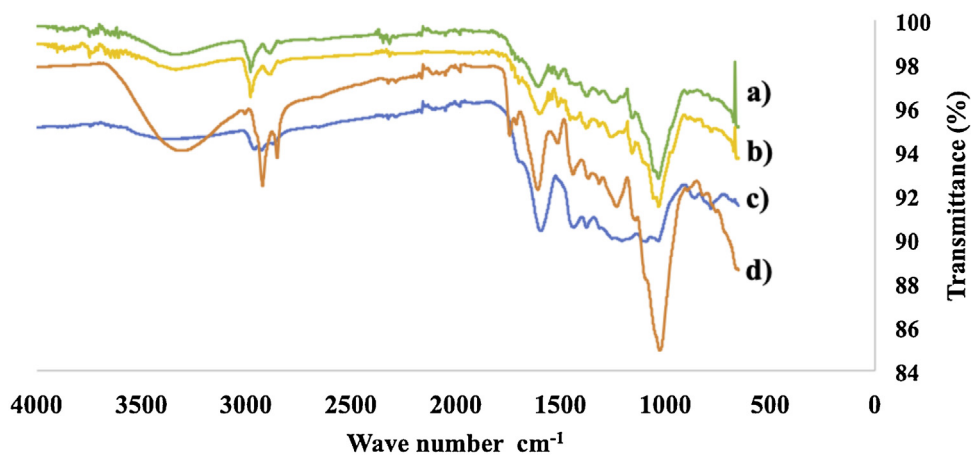


**Fig. 9.** FT-IR spectrum of untreated and treated hazelnut shell samples at different temperatures **a)** 220 °C **b)** 260 °C **c)** Raw Material **d)** 300 °C.

overlapping and combination of aliphatic and aromatic O—H groups [35]. Hazelnut shell is composed of cellulose, hemicellulose and lignin. The bands at $2920\,cm^{-1}$, $2851\,cm^{-1}$ and $1026\,cm^{-1}$ belong to usual cellulose and hemicellulose structures that imply C–H bending of alkanes, saturated aliphatic C–H bending and beta- glycosidic bond, respectively [29,36]. The absorption at 1400 and $1600\,cm^{-1}$ shows the lignin (benzene ring) in the raw material [35]. In addi-

tion, peak at the $1605\,cm^{-1}$ refers to C=C aromatic stretching bond and peak 1742 shows C=O stretching in ketone, esters group. Peaks at 2920, 2851 and $1026\,cm^{-1}$ almost disappeared at 300 °C. This is because of the degradation of hemicellulose and cellulose with the supercritical ethanol-acetone mixture. The absorption peaks at 1400 and $1600\,cm^{-1}$ did not disappear at all temperatures. It means that lignin did not completely decompose at these temperatures.
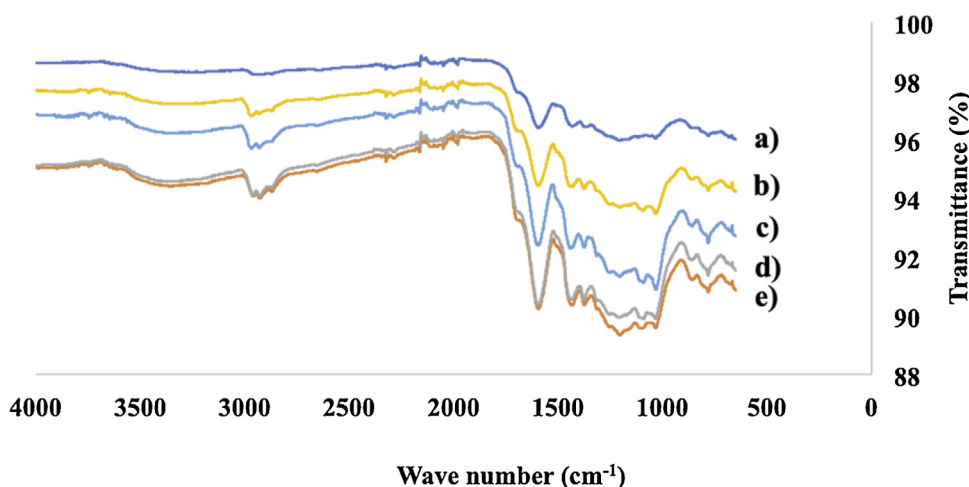
**Fig. 10.** FT-IR spectrum of untreated and treated hazelnut shell samples with different ethanol/acetone (v/v) at 300 °C **a)** 0:100 **b)** 75:25 **c)** 100:0 **d)** 50:50 **e)** 25:75.

## 4. Conclusion

Reaction temperature, time and different ethanol/acetone (v/v) ratios were determined as the effective process parameters in achieving high conversion and bio-oil yield in thermochemical conversion of hazelnut shell waste. By increasing temperature, conversion and bio-oil yield were increased significantly for each solvent type. However, increment of time did not affect the conversion and bio-oil yield as the temperature did. 50/50 (v/v) ethanol-acetone mixture gave the highest bio-oil bio oil yield by showing synergetic effects. Highest solid conversion and bio-oil yield were found as 64.2% and 44.2 wt.%, respectively. According to GC–MS results, ethyl oleate was the major compound for all solvent ratios, whereas for pure acetone oleic acid was the main component. Parameters effects were also investigated by using statistical analysis. All individual parameters have significant effect on conversion and bio-oil yield as well as time-temperature as two-way interactions. However, time-ratio and temperature-ratio did not show significant effects.

## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.supflu.2019.03.019.

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