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INSTITUTE FOR GRADUATE STUDIES
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PYROLYSIS OF APRICOT KERNEL AS A BIOMASS WASTE AND ANALYSIS OF PRODUCTS

BÖRÇE TUNÇOK

MASTER THESIS

Department of Chemical Engineering

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Prof. Dr. Fatma Karaca ALBAYRAK

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BÖRÇE TUNÇOK

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ÖZET

Bu çalışmada, biyokütle atık maddesi olarak kayısı çekirdeği ile piroliz çalışması gerçekleştirilmiştir. Sıcaklık 350-650^oC, reaksiyon süresi 10-50 dakika ve süpürme gazı debisi 150-450 ml/dakika şartlarında çalışılarak, işlem koşullarının toplam dönşüm ile sıvı, katı ve gaz ürün verimleri üzerindeki etkileri incelenmiştir. Deneylerde, 40^oC/dakika sabit ısıtma hızında, azot gazı atmosferi altında, elektrik ile ısıtılan yatak silindirik bir fırın kullanılmıştır.

Çalışmann ilk aşamasında, seçilen deneysel parametrelerin bireysel etkileri incelenmiştir. İkinci aşamada, seçilen deneysel parametrelerin verimler üzerindeki etkileri Box-Behnken deneysel tasarım yöntemine uygun olarak araştırılmıştır. Bağımsız değişkenlerin 3 seviye üzerinden piroliz verimleri üzerindeki etkileri araştırılmıştır. Son aşamada ise elde edilen katı ürünlerin FTIR ve SEM, sıvı ürünlerin ise FTIR analizleri gerçekleştirilmiştir.

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ABSTRACT

In this study, pyrolysis of biomass waste material, namely apricot kernel shell, was carried out. Temperature, reaction time and sweeping gas flowrate were the parameters whose effects on liquid, solid and gas yields and total conversion were studied at the intervals of 350-650^{o}C, 10-50 min and 150-450 ml/min, respectively. The experiments were conducted in an electrically heated horizontally placed cylindirical furnace, under nitrogen atmosphere at a fixed heating rate of 40^{o}C/min.

In the first part of the study, the individual effects of selected parameteres were investigated. In the second part, multivariate analyses were performed by using Box-Behnken experimentad design method. The independent variables and their effetcs on pyrolysis yields were studied at the three levels (-1,0 and 1). Finally, the FTIR and SEM analyses were done on the solid products and the FTIR analyses were done on the liquid products of pyrolysis studies.

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SYMBOLS

B :Amount of Biomass Waste Material (gr)

F :Rate of Mean Square of Model to Mean Square of Remain

F_{chart} :F Value from the Chart

G :Yield of Gas Product (% wt.)

K :Factor Number

k :Constant of Rate (dk^{-1})

L : Yield of Liquid Product (% wt)

MS :Mean Square

MS_{model} :Mean Square of Model

n : Experiment Number, Degree of Experiment

n_0 :Repeated Experiment Number at the Center

N :Necessary Experiment Number

p : Fraction Number

Q_{S1} : Weight of Solid Product(gr)

Q_{S2} :Weight of Solid Product on the Quartz Pipe (gr)

Q_{SL1} :Weight of Quartz Pipe with Solid and Liquid product (gr)

Q_{SL2} :Weight of Quartz Pipe with Solid Product (gr)

Q_{L1} :Weight of Liquid Product (gr)

Q_{L2} :Weight of Liquid Product on the Quartz Pipe(gr)

R :Gas constant , Correlation Parameter

R^2 :Correlation Coefficent

RT :Reaction Time (min)

S	:Yield of Solid Product(%wt)
SGR	: Sweeping Gas Rate (ml/min)
$\mathbf{SS_{model}}$	:Total Square Sum of Model
SS_{T}	:Total Square Sum
T	: Temperature (ºC, K)
TC	: Total Conversion (% wt.)
x	:Independent Variable
X	:Coded Level Matrix
x_1	:Coded Value of Temperature
x_2	:Coded Value of Reaction time
x_3	:Coded Value of Sweeping Gas Rate
X^t	:Transpoze of X Matrix
y	:Respond Value
y_J	:Experimental Value
$\hat{y}_J$	:Acquired Value from Model Equation
Y	:Variable, Respond of the System
$\mathbf{Y_L}$	:Model Equation for Liquid Product Yield
$\mathbf{Y_G}$	:Model Equation for Gas Product Yield
$\mathbf{Y_S}$	:Model Equation for Solid Product Yield
$\mathbf{Y_{TC}}$	: Model Equation for Total Conversion
$\boldsymbol{\beta}$	:Unknown coefficient, Heating Rate

ABBREVIATIONS

ASTM: American Society for Testing and Materials

BP:British PetroleumCompany

DTA: Differential Thermal Analysis

FAO : Food and Agriculture Organization

FTIR :Fourier Transform InfraRed

PID: Proportional Integral Derivative

SEM: Scanning Electron Microscope

TG : Thermogravimetry

WEC :World Energy Council

WECTNC: World Energy Council Turkish National Commitee

FIGURE LIST

TABLE LIST

1. INTRODUCTION

Energy is the driving force for the development of world economy. Fossil fuels such as petroleum, coal and natural gas satisfy the major fraction of total need of world's energy. According to the statistical evaluations, of the world energy demand, % 34.1 oil that meets 40.5 years, 26.5% of the coal that meets 147 year and 20.9% of natural gas that meets 63.3 years can be only used for these years (BP, 2007; WECTNC, 2009). While oil consumption which meets the high demand of world primary energy supply is 2807 million tons in 1985, this value with the average annual growth rate of % 1.5 in 2008 has reached 3928 million tons (Balat and Balat, 2010). The rapid decline in the amount of the reserve, the increase in consumption and some political approaches, affect oil prices. These fluctuations have affected both the industry and the social life adversely (Açıkalın, 2010).

However, the burning of fossil fuels causes green house gas emission which has many divers role to the environment. In addition, the deposition of fossil fuels is limited. But the demand of energy is growing at high rate due to the development of all aspects of the world. To meet the growing demand of energy and to help solve the environmental problems, the world trends are moving towards sustainable energy production, reduced vehicle and industrial pollution, green house gas and waste minimization and distributed electricity generation.

The renewable energy types whose sources are alternative to fosil fuels, can mainly be classified as biomass energy, hydropower, geothermal energy, solar energy and wind energy. Among these sources, biomass is often believed to have the highest potential to contribute to a futuru sustainable energy supply, due to the following advantages: it is one of the most abundant renewable resources and is the fourth largest energy source in the world; it represents the only source of liquid, solid and gaseous fuels in contrast to other renewable energy sources that give heat and power; its usage for energy production solves in part the waste disposal problem, and its conversion to fuels causes minimal environmental problem

Technologies for the thermochemical conversion of biomass to transportation fuels have recently received increased interest from the scientific community, governments, and industry. This renewable energy source has the potential to displace petroleum-derived fuels and as a result offers benefits to many countries. Thermochemical biofuels can often be produced locally and can improve a country’s trade balance and improve national security. Local agricultural industries can be supported, and since these approaches typically use the lignocellulosic materials contained in agricultural residues, forest byproducts or municipal waste, the impact on food production can be minimized. Finally, since the plant matter used in these processes is produced by the photosynthetic reduction of carbon dioxide, utilization of biofuels can essentially be carbon neutral with respect to the build up of atmospheric greenhouse gases. As a result of these benefits of biofuels governments have set a number of ambitious goals regarding biofuels utilization. Significant research effort is underway to help make thermochemical technologies more cost effective (Bahng et al., 2009).

Pyrolysis and gasification are two of the more promising utilization methods for the conversion of biomass toward a clean fuel source. In pyrolysis, biomass is heated to moderate temperatures, 400–700 ◦C, in the absence of stoichiometric oxygen to produce oil that can be used as a feedstock in existing petroleum refineries (Bridgwater,1999; (Bridgewater,2002; Bridgewater,2005).

This is a high throughput processes that has the potential for requiring relatively low capital investment. In gasification, biomass is heated to high temperatures, >700 ◦C, to produce a synthesis gas (H_2 and CO), which can be converted in a catalytic step to liquid transportation fuels (mixed alcohols, Fischer-Tropsch fuels, methanol-to-gasoline, etc.).

The gasification of biomass for power generation has some disadvantages such as it needs coupling between gasification and power generation units and the difficulty of storage, transportation and handling of gaseous fuels. Liquid fuel (bio-oil) has some advantages in transport, storage, combustion, retrofitting and flexibility in production and marketing. The bio-oil is a mixture of about 200 types of major and minor organic compounds and this can be used as a source of some pure chemicals such as alcohol, phenol, aldehyde, organic acids, etc. As a fuel it can be directly used in engine, turbine and furnace withsome modification of equipment. (Bridgwater, 2005)

Pyrolysis has been introduced and offers the advantages of a liquid product bio-oil – that can be readily stored and transported, and used as a fuel, an energy carrier and a sorce of chemicals. Bio-oils have been success fully tested in engines, turbines and boilers, and have been up graded to high quality hydro carbon fuels although at a presently unacceptable energetic and financial cost. Pyrolytic oil can be stored for long periods of time, and is therefore available when necessary. Transportation of pyrolysis oil is very convenient. Existing infrastructure can be used for transportation of pyrolytic oil.

Pyrolytic oil can be used in applications where it substitutes for crude oil, doing so it offers a unique way to reduce dependency on fossil fuels. Just like fossil fuels, bio-fuels are burned in internal combustion, jet or even steam engines to provide power to move everything from pistons to turbines. Slow pyrolysis is also known as conventional pyrolysis. Several literatures revels that in case of pyrolysis the yield of oil is less and char yield is more. Conventional pyrolysis involves all three types of pyrolysis product (gas, liquid, and char). The slow pyrolysis of pomegranate seeds was carried out by Uçar and Karagöz at 400, 500, 600 and 800 ^{o}C to know the effect of temperature on the product distribution. The maximum liquid yields were obtained at the temperatures of 500 and 600 ^{o}C (Uçar and Karagöz, 2009). Beis et al. studied the pyrolysis behavior of safflower seed in fixed-bed pyrolyzer. They obtained the maximum oil yield of 44% at temperature of 500^{o}C, particle size range of +0.425– 1.25 mm, with heating rate of 5 ^{o}C/min and sweep gas (N_2) flow rate of 100 cm3/min (Beis et al., 2002). Şensöz et al., studied the safflower (Charthamus tinctorius L.) seed press cake in fixed bed reactor at 400 - 600 ^{o}C temperature, at 10, 30, 50 ^{o}C/min different heating rate under the sweep gas of N_2 with a flow rate of 100 cm^3/min to investigate the effects of pyrolysis temperature, heating rate and sweep gas flow rates on the yields of the products. They obtained the maximum yield of bio-oil 36% by weight at 500 ^{o}C with a heating rate of 50 ^{o}C/min under the sweep gas of N_2 with a flow rate of 100 cm^3/min (Şensöz and Argın, 2008). Pyrolysis behavior of cotton-seed cake was studied by Putun et al. under catalyst at different conditions and investigated the effect of pyrolysis temperature, catalyst and sweeping gas flow rate and concluded that maximum 30.84% of liquid yield at temperature of 550 ^{o}C, sweeping gas flow rate of 100 cm3/min in the presence of catalyst (20% based on raw material) (Pütün et al., 2006) Rapeseed cake was pyrolyzed by Karaosmanoglu and Çulcuoglu in a fixed bed stainless steel reactor from temperature 450 to 850^{o}C under static atmosphere at rates of 15 ^{o}C/min and 25 ^{o}C/min towards understanding the influence ofheating rate and pyrolysis temperature on product yield. The maximum yield was obtained at 650^{o}C at a heating rate of 15^{o}C/min (Karaosmanoglu and Culcuoglu,2001). Pyrolysis experiments on soybean cake was carried out by Uzun et al. in a fixed-bed reactor under nitrogen and steam atmosphere and obtained the maximum yield of oil 33.78% at 550 ^{o}C of particle size 0.850 > Dp < 1.250 mm when sweeping gas (N_2) flow rate was 200 cm3/min and the oil yield increased to 42.79% with a steam velocity of 1.3 cm/s (Uzun et al., 2006. The effect of particle size on the yields of the pyrolysis products was investigated by Sensoz et al. on Brassica napus L. İn a Heinze reactor under static atmosphere at a temperature of 500 ^{o}C at 40 ^{o}C/min of heating rate with a particle size of range of 0.224–1.8 mm, maximum 46 wt.% oil obtained with a particle size range of 0.85–1.8 mm with a heating value of 38.4 MJ/kg (Şensöz et al., 2000).

Rapeseed Pyrolysis were performed by Onay and Kockar in a free fall reactor at atmospheric pressure under nitrogen atmosphere. The maximum pyrolysis conversion was obtained as 78% at a temperature of 700 ^{o}C. The maximum bio-oil yield of 75% was obtained at a final pyrolysis temperature of 600 ^{o}C, particle size range of 0.224–0.6 mm and the sweep gas flow rate of 100 cm3/min (Onay and Kockar, 2006). Putun et al. studied the rapid and slow pyrolysis of pistachio shell and concluded that the highest bio-oil yield with a value of 27.7% at a temperature of 773 K when the heating rate and carrier gas flow rate were as 300 K/min and 100 cm3/min respectively (Pütün et al. 2007). Cao et al. studied the slow pyrolysis of waste corncob, observed a faster rate of production at a temperature range of 350–400 ^{o}C and a slower at 400–600 ^{o}C whereas the yield of the liquid was nearly constant (Cao Q et al., 2004)

In this study, the effect of the various experimental parameters on the pyrolysis of biomass waste material, namely apricot kernel, were investigated both individualy and statistically. The products were analyzed by using some analytical techniques for characterization.

2.APRICOT

2.1 Apricot

Apricot (Prunus armeniaca L.) is classified under the Prunus species of Prunoidae sub-family of the Rosaceae family of the Rosales group (Gökbulut, 2012). The important cultivars of apricot grown in Malatya province in eastern Anatolia are classified as Hacıhaliloglu, Kabaası, Hasanbey, Sogancı, and Cataloglu and this region is the biggest export center for dried type of apricot in Turkey as 80–85% of world's apricots are exported from here.(Erdoğan-Orhan, 2011).

The apricot fruits are a rich source of oil, protein, soluble sugars, fiber aswell as fatty acids, carotenoids such as β-carotene, β-cryptoxanthin, γ-carotene, and lycopene, phenolics such as chlorogenic and neochlorogenic acids, (+)-catechin and (−)-epicatechin, and rutin, pectin and mineral elements including Na, P, K, Ca,Mg, Fe, Zn, Mn, and Cu (Erdoğan-Orhan,2011).

Hacıhaliloglu type apricot kernels contain 17.38% protein, 48.70% crude oil, 3.68% Na, 1.06 ppm P, 0.58 ppm K, 0.11 ppm Ca, 0.24 ppm Mg, 42.8 ppm Fe, 42.35 ppm Zn, 1.10 ppm Mn, 2.09 ppm Cu (Gezer, 2002).

Apricot is very important for human nutrition, this fruit can be utilized fresh, dried or processed and the kernels are used in the production of oils, benzaldehyde, cosmetics, active carbon, and aroma perfume.

2.1.1 Apricot production in Turkey

Turkey is the biggest apricot producer in the world with 716.415 ton production and 20.6 % share. Moreover, 79.7 % of dried apricots in the world markets are produced in Turkey (FAO, 2010). There are 13.859.671 apricot trees, of which 10,710,000 are fruit-bearing and 2.499.2900 are non-bearing (SSI, 2011).

The province of Malatya in Turkey is the main production area in Turkey; the ‘‘sweet’’ whole dried apricots are unique in the world. Today, about 50% of fresh apricot production and 95% of dried apricot production in Turkey is provided from Malatya. Therefore, it is an important apricot production center, not only for Turkey but also for the whole world. Substantial quantities (90–95%) of dried apricots are exported, especially to European countries, and about 80% of the world's dried apricots are produced in Malatya. The monetary contribution of apricot export to the Turkish economy was 152 million dollars in 2003. In the same year, 227504 tons of fresh and 50025 tons of dry apricot were produced from 6083000 apricot trees in the Malatya province. (Esengün, 2007)

Table 2.1 Apricot production in Turkey

Year	Area of compact fruits (decare)	Productions (tons)	Average yield of per tree(kg)	Number of bearing trees	Number of non bearing trees	Total number of trees
2007	967.658	557.572	44	12.605.467	2.288.088	14.893.555
2008	1.020.292	716.415	54	13.261.418	2.200.198	15.461.616
2009	1.040.561	660.894	49	13.489.693	2.221.379	15.711.072
2010	1.080.534	450.000	33	13.769.675	2.314.970	16.084.645
2011	1.120.793	650.000	47	13.859.671	2.499.290	16.358.961

Table 2.2 Marketing details of apricot in Turkey

Marketing Year	2010-2011	2009-2010	2008-2009	2007-2008	2006-2007
Production (Tons)	476.132	660.894	750.574	589.732	483.459
Harvest losses (Tons)	19.998	27.758	31.524	24.769	20.305
Supply=use (Tons)	461.297	635.135	721.880	568.775	468.474
Usable production (Tons)	456.134	633.136	719.050	564.963	463.154
Imports (Tons)	5.163	1.999	2.830	3.812	5.320
Imports from EU 27(Tons)	2.316	1.023	2.442	2.651	...
Domestic use(Tons)	24.341	127.794	225.949	70.432	90.285
Human consumption (Tons)	22.394	117.571	207.873	64.797	83.062
Losses (Tons)	1.030	10.224	18.076	5.635	7.223
Exports (Tons)	453.968	510.031	491.106	513.526	546.464
Exports to EU 27(Tons)	179.035	192.327	198.105	202.774	...
Change in stocks (Tons)	-17.012	-2.690	4.825	-15.183	-168.275
Human consumption per capita	0,3	1,62	2,91	0,92	...
Degree of self - sufficiency (%)	1873,9	495,43	318,24	802,14	512,99

2.1.2 Apricot production in the world

Total fresh apricot production is almost 3,500,000 tones anually in the world, approximately 700,000 tones of this amount are made by Turkey. Turkey is the first country with 20% rate of the world apricot production. Turkey is followed by Iran (8%), Uzbekistan (7%) and Italy(6%) .

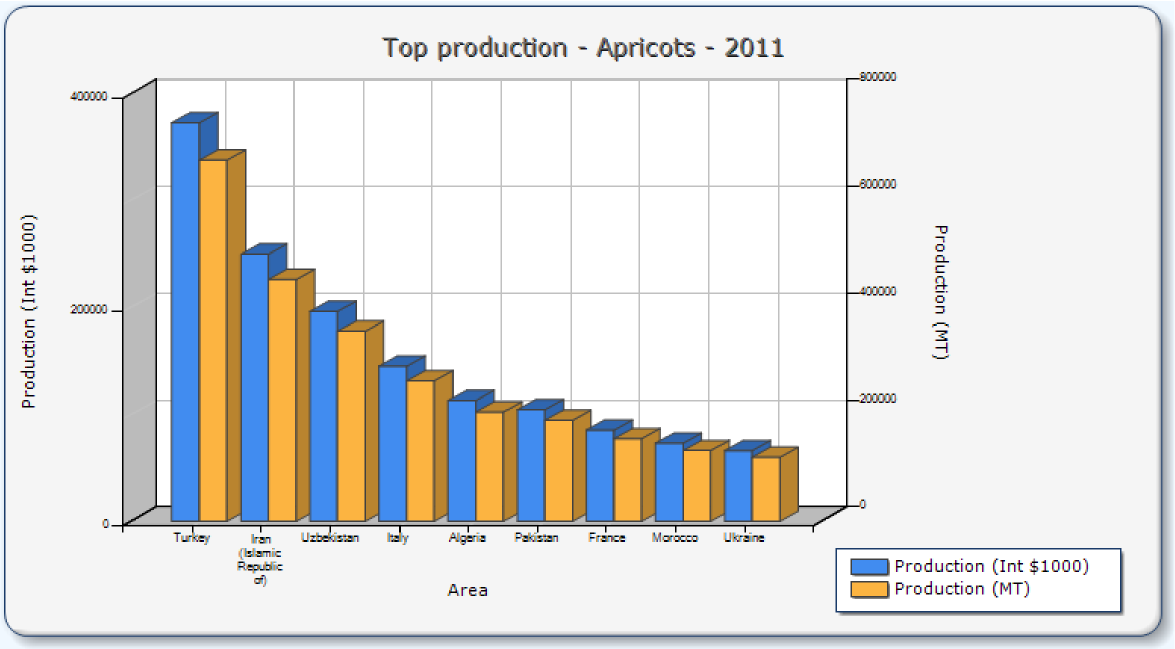


Figure 2.1 Apricot production in the world (FAO, 2011)

Germany (19,3 %), Russia (19,10 %) and Italy (10,80 %) are leading countries in the fresh apricot import market and in the Export market France (25,7 %), Spain (12,8%), Greece (8,90 %) and Turkey(8,20%) are leading countries. Import and export values of fresh apricot in the world are shown in Table 2.3 and Table 2.4 in turn.

Table 2.3 Import values of fresh apricot in the world

	2003	2004	2005	2006	2007	2007%
GERMANY	33.588	40.289	50.192	50.372	35.406	19.30%
RUSSIA	11.957	22.869	32.923	59.125	34.984	19.10%
ITALY	24.699	22.034	20.441	28.962	19.791	10.80%
FRANCE	11.531	7.374	10.297	11.498	8.919	4.90%
WORLD	16.124	170.964	213.478	250.438	183.099	100%

Table 2.4 Export values of fresh apricot in the world

	2003	2004	2005	2006	2007	2007%
FRANCE	34.254	49.989	57.777	62.558	46.477	25.70%
SPAIN	41.551	21.252	39.064	47.811	23.221	12.80%
GREECE	5.129	11.207	14.901	14.096	16.178	8.90%
TURKEY	6.075	7.931	9.844	13.956	14.897	8.20%
ITALY	9.897	13.711	14.432	11.777	11.604	6.40%
USA	8.949	6.945	6.053	3.787	7.467	4.10%
WORLD	152.84	166.57	207.411	248.808	180.856	100%

Russia (27,9 %), USA (11,3 %) and England (7,90 %) are leading countries in the dried apricot import market and in the export market Turkey (80,6 %), France (2,20 %), Uzbekistan (2,10 %) are leading countries. Import and export values of dried apricot in the World are shown in Table 2.5 and Table 2.6 in turn.

Table 2.5 Import values of dried apricot in the world

	2003	2004	2005	2006	2007	2007%
RUSSIA	23.164	26.903	30.418	41.87	40.203	27.90%
USA	14.78	16.263	14.632	18.139	16.319	11.30%
ENGLAND	8.546	11.146	10.651	11.943	11.358	7.90%
GERMANY	7.034	7.896	8.929	9.358	9.95	6.90%
FRANCE	7.287	8.818	8.649	8.777	8.153	5.70%
WORLD	99.039	112.966	120.895	144.257	143.88	100.00%

Table 2.6 Export values of dried apricot in the world

	2003	2004	2005	2006	2007	2007%
TURKEY	71.9	81.292	96.019	113.86	105.31	80.60%
FRANCE	2.358	2.891	3.472	3.221	2.907	2.20%
UZBEKISTAN	2.533	1.245	1.674	2.844	2.775	2.10%
GERMANY	795	1.441	1.721	2.676	2.414	1.90%
IRAN	1.91	1.245	751	3.468	600	0.50%
WORLD	90.395	99.018	115.226	137.785	13.376	100%

2.2. Apricot Kernels

In our country, apricot kernels mainly come out in the waste of the industry of juice, jam, cake, dried fruit and the waste of the processing plant of apricot domestic waste. Obtaining an exact amount of shell waste is impossible. Moreover, we can obtain an estimated value by using the product/shell rate with production amount. it can be estimated that the amounts of apricot kernels are 650.000 tones average values per year.

These wastes are used especially as fuel in our country, however, they are thought to have an enormous potential as chemical raw material and fuel.

3. STATISTICAL ANALYSIS

Statistics is the study of the collection, organization, analysis, interpretation, and presentation of data. Methods based on numerical measurement are improved and applied theoretically. These methods are applied for planning and designing experiments aimed for research. Statistical methods are frequently used in studies because using minimal time, money and materials and getting minimum mistake is of vital importance. It is stated that statistically designed experiments yield almost ten times more when considering laboratory and time (Karaca, 2000 and Açıkalın 2010). It can be applied in almost every branch, especially in biology, physics, chemistry, engineering, economics, astronomy, psychology, sociology, agriculture and transportation.

3.1 Experimental Design

The use of experimental design methods in the chemical industry was promoted in the 1950s by the extensive work of Box and his collaborators on response surface designs (Box and Draper, 1987)

Experimental design is the first and the most important step in statistical analysis. It is used for identification, characterization of factors affecting process and improvement of process's experimental model. Used experimental design technique provide to specify the behaviour of the process by providing maximum information with minimum number of experiment. It is possible to determine the alterations required to be made along with providing information about the process by changing the factors which are expected to be effective in process behaviour within the frame of design made . also provides a full insight of interaction between design element (Cochran and Cox, 1957, Açıkalın, 2010).

In an experiment, a researcher manipulates one or more variables, while holding all other variables constant. By noting how the manipulated variables affect a response variable, the researcher can test whether a causal relationship exists between the manipulated variables and the response variable. Variables that can affect experiment result and be changed independently are called *factor (independent variable)*. All chapters signifying each factor are called *level* and result measurements obtained from experiments are called *answer*. The change that comes out as a result of factor level change is called the *effect* of that factor (Kuehl, 2000).

The choice of an experimental design method depends on the objectives of the experiment and the number of factors to be investigated. It is widely accepted that the most commonly used experimental designs in experimental study are full and fractional factorial designs at two levels and three-levels, central composite rotatable design, Box-Behnken design. In present work, Box-Behnken design method was used as experimental design method.

3.1.1 The Box-Behnken design

The Box-Behnken design is an independent quadratic design in that it does not contain an embedded factorial or fractional factorial design (Ferreira et al., 2007; Zidan et al., 2007). It is defined as a set of experimental designs for response surface methodology that has points at center and the midpoint of each side. Devised by George E. P. Box and Donald Behnken in 1960, these are designed to achieve goals such as: a) each factor, or independent variable, is placed at one of three equally spaced values, b) the design should be sufficient to fit a quadratic model, that is, one containing squared terms and products of two factors, c) the ratio of the number of experimental points to the number of coefficients in the quadratic model should be reasonable and d) the estimation variance should more or less depend only on the distance from the centre, and should not vary too much inside the smallest (hyper) cube containing the experimental points (Khajeh, 2009a; Tripathi et al., 2009).

One advantage of these designs is that they do not include experiments in which all factors are at the highest or lowest level synchronously. In other words, it doesn’t require an experiment in the corner points of its study area. In this work, as mentioned before, the experimental design to be used was chosen as Box-Behnken Experimental Design. The Box-Behnken designs are three-level incomplete factorial designs for exploring second order response surfaces (Hinkelmann and Jo,1998) In this design, the treatment combinations are at the midpoints of edges of the process space and at the center. Figure 3.1 illustrates a Box-Behnken design for three factors. The experiments to be performed are composed of the experiments which were performed at the center of each side of the cube and at the center of the cube. (Ragonese et al., 2002; Guo et al., 2008).

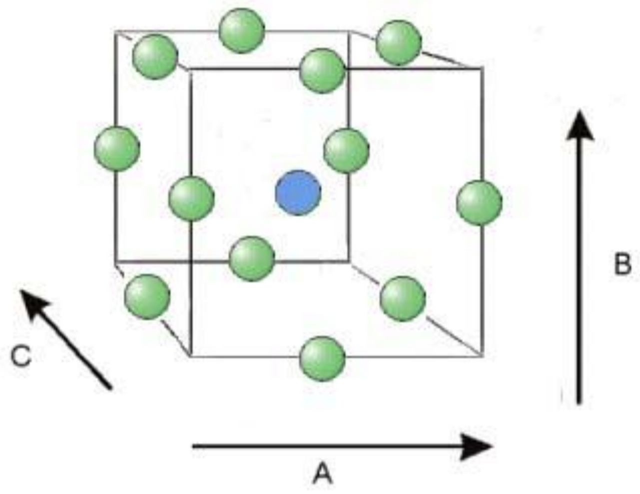


Figure 3.1 A symbolic indication of triple factor Box-Behnken design(Açıkalın, 2010)

The coded values of factors were calculated from the original values with the help of the formula given by Draper and Smith (Draper and Smith, 1981):

x = (original value - midpoint value)/ interval value

Box-Behnken Design is a triple level design and the coding is -1, 0 and +1. Necessary experiment number for design is *(N),* the number of factor is *k* and repeated experiment number at the center is n_0 and then it is calculated as in the following; $N = 2k\,(k\text{-}1) + n_0$.

3.2 Regression Analysis

Regression analysis is an appliance which is used for searching the relation between one or more dependent variables (x_1, x_2, x_3...., x_k) and one and continuous dependent variable (Berk, 2004; Kleinbaumand et al., 2008). Regression in which one independent variable is used, is called *single variable regression analysis* and regression analysis in which more than one independent variable is used, is called *multivariate regression analysis* (Berk, 2004; Kleinbaumand et al., 2008). If the relation between dependent and independent variables is linear, it is called *linear regression*, but if it is not linear, it is called non-linear regression.

In regression analysis, a system of equations is created that reflects the relation between dependent and independent variables and signifies the power and form of the relation. For example, if it is assumed that *n* pieces experiments are performed for *k* pieces experiments, the result will be as below:

$y_1, y_2, \ldots.., y_n,$

$$\begin{aligned} y_1 &= \beta_1 x_{11} + \beta_2 x_{21} \ldots\ldots\ldots \beta_k x_{k1} + \varepsilon_1 \\ y_2 &= \beta_1 x_{12} + \beta_2 x_{22} \ldots\ldots\ldots \beta_k x_{k2} + \varepsilon_2 \\ &\vdots \\ y_n &= \beta_1 x_{1n} + \beta_2 x_{2n} \ldots\ldots\ldots \beta_k x_{kn} + \varepsilon_n \end{aligned} \tag{3.1}$$

If these equations are written as matrix,

$$Y = \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_n \end{bmatrix}_{n\times 1} \quad X = \begin{bmatrix} x_{11}x_{21}\ldots\ldots\ldots x_{k1} \\ x_{12}x_{22}\ldots\ldots\ldots x_{k2} \\ \vdots \\ x_{1n}x_{2n}\ldots\ldots\ldots x_{kn} \end{bmatrix}_{n\times k} \quad \beta = \begin{bmatrix} \beta_1 \\ \beta_2 \\ \vdots \\ \beta_k \end{bmatrix}_{k\times 1} \quad \varepsilon = \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \vdots \\ \varepsilon_n \end{bmatrix}_{n\times 1}$$

these results are acquired. Based on these matrixes, model equation parameter is acquired from

$$\beta = (X^t \cdot X)^{-1} \cdot X^t \cdot Y \tag{3.2}$$

(Sen and Srivastava, 1990; Açıkalın, 2003). *X* is coded level matrix and X^t is the transposition of *X* matrix.

3.3. Model Equation Control

Some statistical analysis are needed to be applied for determining how much available acquired regression model equation is such as sum of residuals, correlation coefficient, variance analysis (Box and Draper, 1987; Hogg and Ledolter, 1989).

3.3.1 Sum of residuals

Sum of residuals is the sum of difference between y_j (observed value in experiments) and $\hat{y}_j$(acquired from model equation) and it must be zero. It is expressed as below in mathematics ((Box and Draper, 1987)

$$\sum e_j = \sum(y_j - \hat{y}_j) = 0 \tag{3.3}$$

3.3.2 Correlation coefficient

Correlation coefficient is a favorite term in statistics and it is used for specifying and measuring if two random variables comply with each other linearly. Correlation coefficient (*R)* reveals deviation point of value acquired from model ($\hat{y}_j$) and experimental value from average value of experimental results and it is found by this equation (Miller et al., 1990)

$$R^2 = \frac{\sum(\hat{y}_j - \bar{y})^2}{\sum(y_j - \bar{y})^2} \tag{3.4}$$

3.3.3 Variance analysis

Variance analysis (ANOVA) is a technic created for experimental result analysis involving quantitative measurements and for making a decision about acquired model. Total variation of experimental results is categorized as intergroup (model) factor variance and in group (residual or error) factor variance. Making a variance analysis can be summarized as below (Sahai and Ageel, 2000; Wang and Jain, 2003):

- The answers obtained for *n* piece observation are y_i and average value of obtained answers in experiments is $\bar{y}$ and Grandtotal of Total Squares SS_T is calculated by the help of formula below:

$$SS_T = \sum_{i=1}^{n}(y_i - \bar{y})^2 \tag{3.5}$$

- Then, Grandtotal of Total Squares falls to pieces of variance that is called Grandtotal of Squares according to factors. For example, for a *Q* piece factor:

$$SS_T = SS_A + SS_B + \ldots\ldots + SS_Q = SS_{model} + SS_{residual} \tag{3.6}$$

- Grandtotal of each square is made comparable by dividinginto degree of freedom with itself. New values acquired by dividing into degree of freedom are called mean square (MS). Mean square values poses opportunity to make statistical inference on hypothesis test or point and space scanning ground.

- Mean square value of model (MS_{model}) is divided into Mean Square Value of Residual ($MS_{residual}$) and F is obtained.
- Importance level (significance level) is decided. Most common importance level in hypothesis tests is 95% (significance level is 5%). Deciding 5% significance level means that an acceptable model may even be refused 5%. In other words, a true decision may be regarded as given 95% dependably.
- By regarding freedom level of residuals and model for chosen significance level, F_{chart}($F_{criticism}$) is obtained. $F_{calculated}>F_{chart}$ is necessary for model validity. If this condition is fulfilled, it is thought that derived model equation is available for recognizing the system. If $F_{calculated}<F_{chart}$, significance level is changed or $F_{calculated}$ value may be increased with the remove of some parameters in model equation. If $F_{calculated}>F_{chart}$ condition is not fulfilled, model equation is changed. (Açıkalın, 2010; Karaca, 2000,)

F test can be realized with *p*-value showed in ANOVA charts besides F rate. If test is realized P-value, significance level (a) is compared with *p-value*. For affirmation of model availability, *p-value* must be smaller than a (*p-value<a).*

F significance test can also be used in specifying if each parameter in the model acquired by regression analysis is significant or not. By eliminating insignificant terms from model, $F_{calculated}$value is increased for model. For this purpose, F rate F_{bi} for each parameter is calculated as below:

$$F_{bi} = \frac{b_i^2 (1/C_{ii})}{S_{\exp}^2} \tag{3.7}$$

In this example, b_i is parameter, $S_{\exp}^2$ is pooled experimental variance and C_{ii} is a matrix that is equal to *i* parameter in $[X^tX]^{-1}$ matrix mentioned in chapter 3.2. F_{bi} values calculated with (3.7) equality is compared with $F_{criticism}$ from available table chosen significance level. If $F_{bi}>F_{criticism}$, mentioned parameter is significant and if not, mentioned term is eliminated from model (Açıkalın, 2010).

4. MATERIAL AND METHOD

4.1 Materials

In this study, a biomass waste material, apricot kernel, was subjected to pyrolysis process. Apricot kernels were obtained from a local market of Malatya province which is located in the Anatolia, Turkey. The shells were separated from the nuts, and then milled by using an IKA 11 model analytic mill. Afterwards, they were sieved to obtain a uniform particle size between 1 and 2 mm. Then, the samples were dried under vacuum at 105°C for 2 h. Glass containers were used for storing the prepared samples.

Table 4.1 Proximate and ultimate analyses of apricot kernel

Moisture (original), (%)	4,78
Volatile matter (%, db[a])	79,24
Ash (%, db)	1,70
Fixed Carbon (%, db)	19,06
Calorific value(kcal/kg)	4420
Carbon (%)	49,29
Hydrogen (%)	5,65
Nitrogen (%)	0,58
Oxygen (%)[b]	44,48
Sulfure (%)	-

[a]Dry basis

Moisture, ash and fixed carbon percentages were calculated according to ASTM E871-872, ASTM D1102-84 and ASTM E 872-82 methods, respectively. The calorific values were obtained by IKA C4000 model bomb calorimeter. Proximate analyses were carried out at TUBİTAK MAM. The results were given in Table 4.1.

4.2. FTIR Analysis for apricot kernel

Fourier transform infrared spectroscopy (FTIR) spectra of solid and liquid products were obtained by using a Perkin Elmer Spectrum One FTIR spectrometer in the Department of Chemical Engineering at Marmara University. The solid products were finely powdered, mixed with KBr at 1/100 sample/KBr weight ratio, and then pressed to prepare translucent pellets. Liquid samples were analysed directly without any preparation.

FTIR spectrum of the apricot kernel is given at Figure 4.1. The peak obtained at about 3365.2 cm^{-1} band was due to O-H stretching vibrations in hydroxyl groups. The peaks appeared at around 2969.8 cm^{-1} and 1365.8 cm^{-1} were caused by methylene asymmetric C-H stretching and methyl symmetrical C-H bending, respectively. The peak in 2145.7 cm^{-1} may be reasoned with -C≡C- stretching arising from alkyne groups (Yang and Lua, 2003; Erdik, 2007). 1722.6 cm^{-1} wave long peak arises from C=O in carbonyl groups and it signifies the presence of groups such as acetyl derivatives and aldehyde groups (Fu et al., 2010). The peak in 1640.8 cm^{-1} arises from C=C stretching occurring in olefinic structure (Lua and Yang, 2005). The peak in 1516.4 cm^{-1} arises from aromatic vibration occurring in lignin structure and the peak in 1500-1600 cm^{-1} peaks arise from C=C vibrations in aromatic ring (Lua and Yang, 2004). On the other hand, the peak in 1365.8 cm^{-1} may arise from C-H vibrations in cellulose structure and C-O siringol derivative vibrations (Kues, 2007). The space in 1300- 1000 cm^{-1} range generally points C-O streching and may have arised from alcohol, phenol, ester, anhydride groups (Stuart, 2004). The peak in 1216.9 cm^{-1} may not only point the presence of ester or phenol groups but also interring ether bridge (Serp and Figueiredo, 2009). it can be said that basic groups of apricot kernels are carbonyl, ether, ester, alcohol and phenol which includes oxygen.

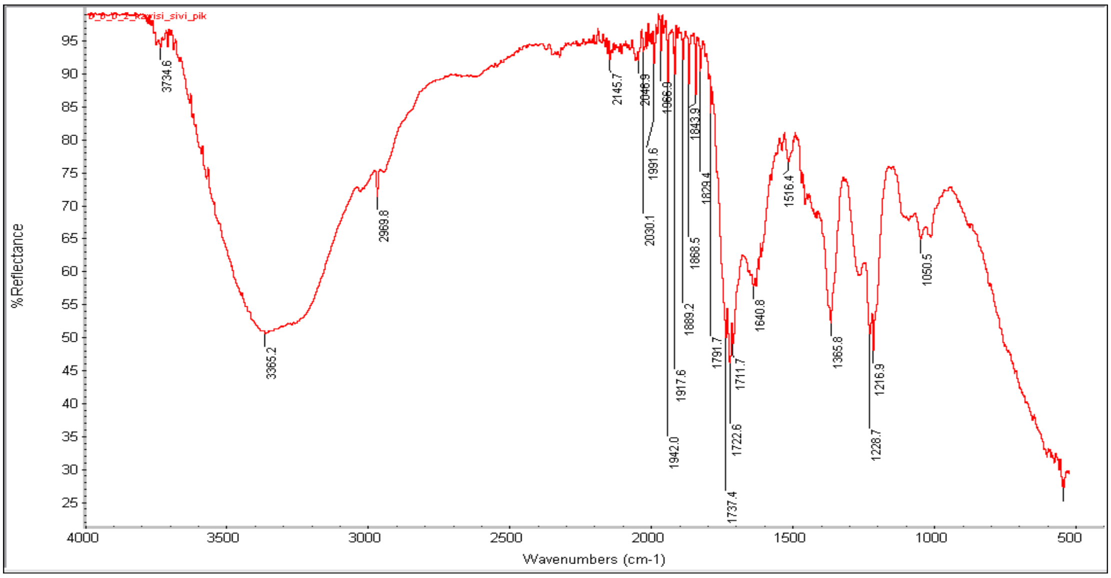


Figure 4.1 FTIR spectrum of apricot kernel

4.3. Thermogravimetric analysis

Thermoanalytical techniques are the most common tools for studying the thermal characteristics and kinetics of biomass pyrolysis. Thermogravimetric (TG) analysis is one of these techniques in which the mass loss of a sample is measured against temperature under controlled heating rate and gas atmosphere, and then recorded in the form of TG curves.

The mass change of apricot kernel over the course of pyrolysis reaction was measured and recorded by Perkin Elmer Diamond TG/DTA system. Apricot kernel samples were ground to particle size <0.1 mm. The samples were dried under vacuum at 105 °C, and kept in glass containers. The experiments were carried out non-isothermally at three different heating rates of 2, 10, and 15°C min^{-1}. Nitrogen at a flowrate of 50 mL/min was used as a carrier gas. In each experiment, a sample mass of 7 ± 3 mg was used. The sample holders were open type platinum pans. The tests were conducted in the 50–900 °C temperature ranges

Figure 4.2 and Figure 4.3 show the TG and the DTG curves of apricot kernels at different heating rates as function of temperature, respectively.

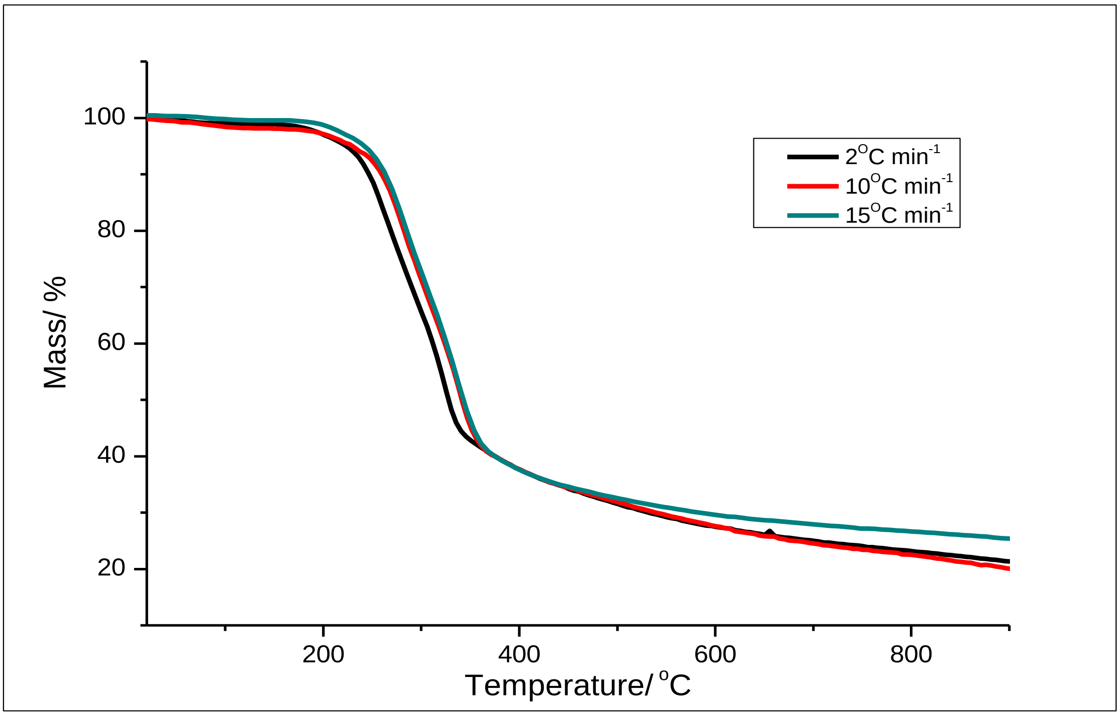


Figure 4.2 TG curves of apricot kernels at different heating rates

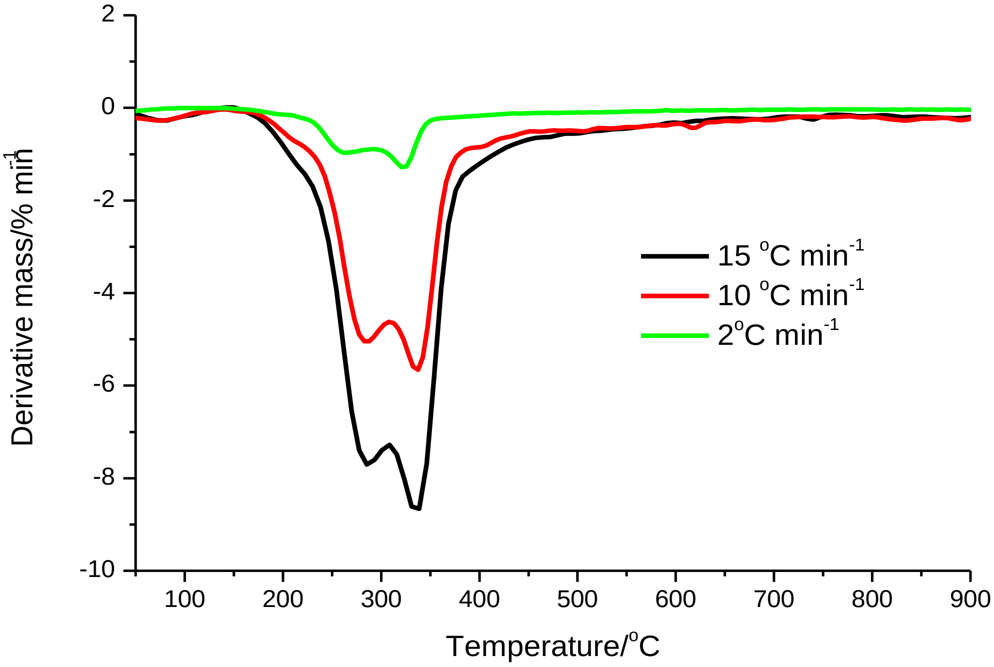


Figure 4.3 DTG curves of apricot kernels at different heating rates

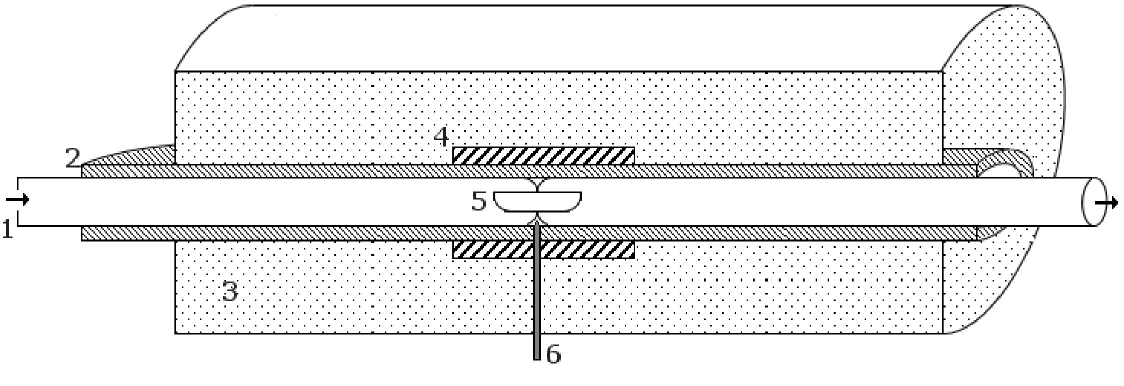
Based on the on the TG curves, the mass loss range can be divided into three zones since every single slope change on a TG curve indicates the beginning of a new zone. The first zone finishes at the 170-200 °C interval with respect to the applied heating rate. This zone represents a slight mass loss which is due to the removal of water present in material and esternal water bounded by surface tension The corresponding area on the DTG curve pyrolysis zone since mass loss is smaller, and the mass loss rate is much lower compared to that in the second zone.

Weight loss at other stages is about hemicellulose, cellulose and lignin content of apricot kernel. It is known that thermal degradation of hemicellulose is realized at 200-260°C, thermal degradation of cellulose is realized at 240-350°C and thermal degradation of lignin is realized at 280-500°C in large measure (Gonzales et al, 2009). On the basis of this information, weight loss at second and third stages can be explained. Second stage is carried out at 220-370°C. Maximum weight loss speed in this stage is approximately 275°C. it can be stated that mentioned weight loss may high probably arise from thermal degradation of hemicellulose and cellulose. Third stage involves 370-800°C and maximum weight loss speed is approximately 340°C. It can be stated that weight loss arise high probably from thermal degradation of cellulose and especially lignin.

4.4 Procedure

The experiments were carried out in a horizontally placed tubular quartz reactor (Fig. 4.4). The length and the inner diameter of the reactor were 102 cm and 4 cm, respectively. The center part (approximately 45 cm) of the reactor was heated electrically. The temperature was measured by a thermocouple which is located just below the sample holder in contact with the quartz tube within an accuracy of ±2 _C, and maintained at the desired value by a PID controller.

For each run, 10 g of apricot kernel sample was placed in a quartz sample holder which has 1 mm diameter holes to promote the escape of vapor/liquid products from sample holder. Next, the sample holder was placed at the center of the reactor to obtain the best heat transfer from furnace to the sample. Two ice-water liquid traps were installed at the reactor exit. After arranging the connections, sweeping gas (nitrogen) was passed through the reactor to remove air/oxygen from reaction medium. Then, the nitrogen flowrate was set to the desired value, and the reactor was heated to the specified reaction temperature at 40 ^{o}C min^{-1}.



1-Quartz pipe 2-Mullit pipe 3-Isolation 4-Heater 5-Sample pot 6- Thermocouple

Figure 4.4 The pipe reactor used in the experiments(Açıkalın, 2010)

Heating was terminated when the desired reaction time was attained, and the system was allowed to cool to room temperature. Thereafter, the sample holder and traps (including their connections) were carefully removed from the reactor, and weighed as

QS1 and QL1, respectively. Later, the reactor involving some liquid and solid products was removed and weighed (QR1). Next, the reactor was washed with tetrahydrofuran to separate the liquid products, and reweighed after drying (QR2). The amount of liquid product in the reactor (QL2) was determined from the difference of QR1-QR2. Likewise, the solid product in the reactor (QS2) was calculated from the difference of QR2 and the empty weight of the reactor. The amount of total liquid (QL) and total solid (QS) products were calculated as QL1 + QL2 and QS1 + QS2, respectively. These values were converted to yields by dividing them with the original amount of biomass. The gaseous product yield was calculated by difference.

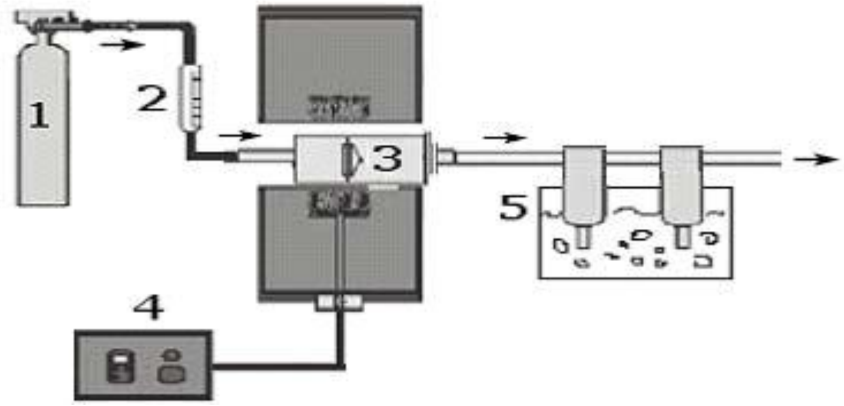


Figure 4.5 The schematics of pyrolysis process.

1)Nitrogen tube 2) Flow meter 3) Reactor 4) PID controller 5) Ice water traps.

5. RESULTS AND DISCUSSION

Since there are many parameters which must be considered in pyrolysis, it appears that it is important to determine the most significant variables affecting the process. In this study, reaction temperature, reaction time and sweeping gas (nitrogen) flow rate were chosen as reaction parameters, and the effects of them on pyrolysis product yield were investigated. Catalyst were not used in experiments. Liquid, gas and solid product yield and total conversion percentages were calculated with the equations below:

Liquid product $(L)\ \% = [L/T]*100$ (5.1)

Gas product $(G)\ \% = [G/T]*100$ (5.2)

Solid product $(S)\ \% = [S/T]*100$ (5.3)

Total Conversion $(TC)\ \% = 100–(S)\% = (L+G)\%$ (5.4)

Here T, is the amount of biomass waste material fed to the pyrolysis process. Liquid, gas and solid products amounts were measured by weight differences on the basis of weighing as it was stated in Section 4.4. The results obtained in the experiments were given in Table 5.1.

Table 5.1. The reaction conditions and the results of experiments for apricot kernel

Run	Temperature (C)	Reaction time (min)	Gas flow rate (ml/min)	Liquid product %	Gas product %	Solid product %	Total Conversion %
1	500	10	150	56	23, 8	20,2	79,8
2	650	30	150	53,1	28,3	18,6	81,4
3	350	30	150	51,6	22,5	25,9	74,1
4	500	50	150	53,1	29,8	17,1	82,9
5	500	10	450	55,7	28,7	15,6	84,4
6	500	50	450	46,2	31,4	22,4	77,6
7	650	30	450	47,2	33,4	19,4	80,6
8	350	30	450	52	18,1	29,9	70,1
9	350	10	300	48,6	21	30,4	69,6
10	650	10	300	53,8	23,9	22,3	77,7
11	650	50	300	48,6	34,3	17,1	82,9
12	350	50	300	48,5	21	30,5	69,5
13	500	30	300	52,5	24,6	22,9	77,1
14	500	30	300	56,5	20,5	23	77
15	500	30	300	50	26,8	23,2	76,8
16	500	30	300	53,1	22,1	24,8	75,2
17	500	30	300	55,5	20,9	23,6	76,4

5.1. Effect of parameters on pyrolysis product yields

5.1.1 Effect of pyrolysis temperature

In this work, the pyrolysis behavious of apricot kernel was investigated with respect to variation of process reaction temperature. Pyrolysis of apricot kernel was carried out at three different pyrolysis temperatures (350, 500 and 650^{o}C) while the reaction time, N_2 flow rate and heating rate were fixed at 30 min, 250 ml min^{-1} and 40^{o}C min^{-1}, respectively. The product distribution as a function of the pyrolysis temperature was given in Table 5.2 and Figure 5.1.

Temperture had a great influence on product yields. The gas product yield and total conversion showed an increase from 15.9% to 28.6% and from 70.8% to 80.8%, respectively, as the pyrolysis temperature was increased from 350^{o}C to 650^{o}C. However, the liquid product yield and solid product yield decreased when temperature increased from 350 to 650^{o}C as expected. Increasing the temperature increased the total conversion because of high moleculer weight's degradation and char's secondary degradation. Also, the gaseous product yield demonstrated a consistently increasing trend with increasing temperature. The increase in gas yield could be attributed to thermal decomposition of apricot kernel and probable thermal decomposition of intermediate solid since the only decreasing yield was solid product yield at the temperature interval of interest.

Unlike gaseous product yield, solid product yield represented a continuous decrease with increasing pyrolysis temperature. This was an expected result since apricot kernel and its intermediate solid product underwent further thermal degradation at elevated pyrolysis temperatures. Other researchers have also observed the same trends for product yields with varying temperatures including the pyrolysis raw materials of pistachio shell [Açıkalın, 2010, Apaydın-Varol and et al., 2007], pomegranate seeds [Uçar and Karagöz, 2009] and soybean oil cake [Şensöz and Kaynar, 2006].

Liquid product yields did not vary with temperature as gas and solid porduct yields. Maximum liquid yield was acquired at 350°C. Because of the conversion of some volatiles into gas products with the secondary degradation reactions liquid product yields decreased when temperature increased.

Table 5.2 Effect of temperature on the pyrolysis product yields

Temperature(ºC)	Liquid product yield	Gas product yield	Solid product yield	Total conversion
350	54,9	15,9	29,9	70,8
500	53,98	22,94	23,08	77,06
650	52,2	28,6	19,2	80,8

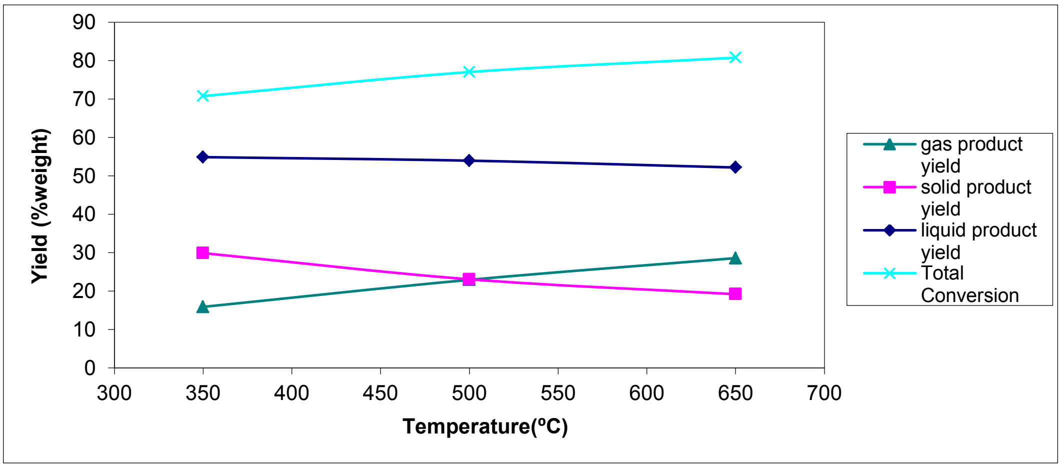


Figure 5.1 Effect of temperature on the pyrolysis product yields

5.1.2 Effect of reaction time on pyrolysis products

Apricot kernel was pyrolyzed at 500°C under 300 ml min^{-1} nitrogen flow rate for 10, 30 and 50 min in order to investigate the effects of reaction time on pyrolysis products. The results were given in Table 5.3 and Figure 5.2.

Table 5.3 The effects of reaction time on pyrolysis product yields

Reaction time (minute)	Liquid product yield	Gas product yield	Solid product yield	Total conversion
10	53,5	22	24,5	75,5
30	53,98	22,94	23,08	77,06
50	56,8	21,2	22	78

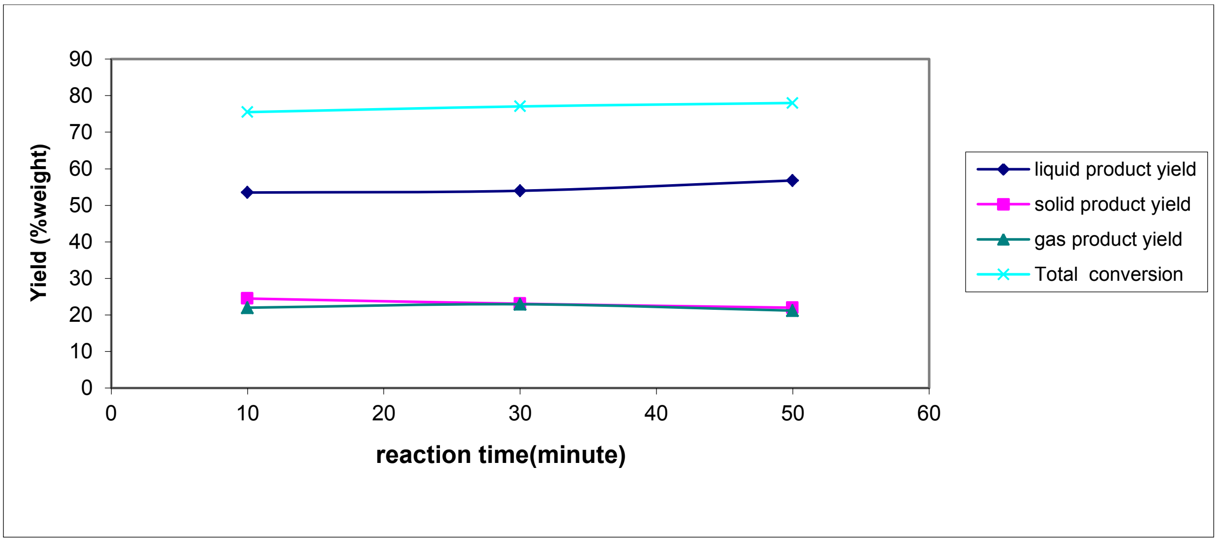


Figure 5.2 The effects of reaction time on pyrolysis product yields

When the effects of reaction time on pyrolysis product yields were analyzed, it was observed that it didn’t have a significant effect on total conversions of apricot kernels (Table 5.3 and Figure 5.2).

Increasing the reaction time from 10 to 50 mins slightly increased the liquid product yield and total conversion. The liquid product yield and total conversion were slightly affected from varying reaction times. On the other hand, the gas yield was almost stable and solid product yield decreased between 30-50 mins. According to the results obtained in this work, the effect of increasing reaction time does not seem to be highly effective on the product yields and total conversion. Based on these result, it can be said that, long term reaction times need to be chosen to obtain high level of liquid product yield.

5.1.3 Effect of sweeping gas (nitrogen) flow rate

Apricot kernel was pyrolyzed under 150, 300 and 450 ml min^{-1} nitrogen flow rate at fixed values of 500^{o}C pyrolysis temperature, 30 min reaction time and 40^{o}C min^{-1} heating rate. Table 5.4 and Figure 5.3 show the influence of N_2 flow rate on product yields.

Table 5.4 The effects of sweeping gas (nitrogen)flow rate on pyrolysis product yields

Sweeping gas flow rate	Liquid product yield	Gas product yield	Solid product yield	Total conversion
150	57,1	19,1	23,8	76,2
300	53,98	22,94	23,08	77,06
450	54,3	33,14	22,9	77,1

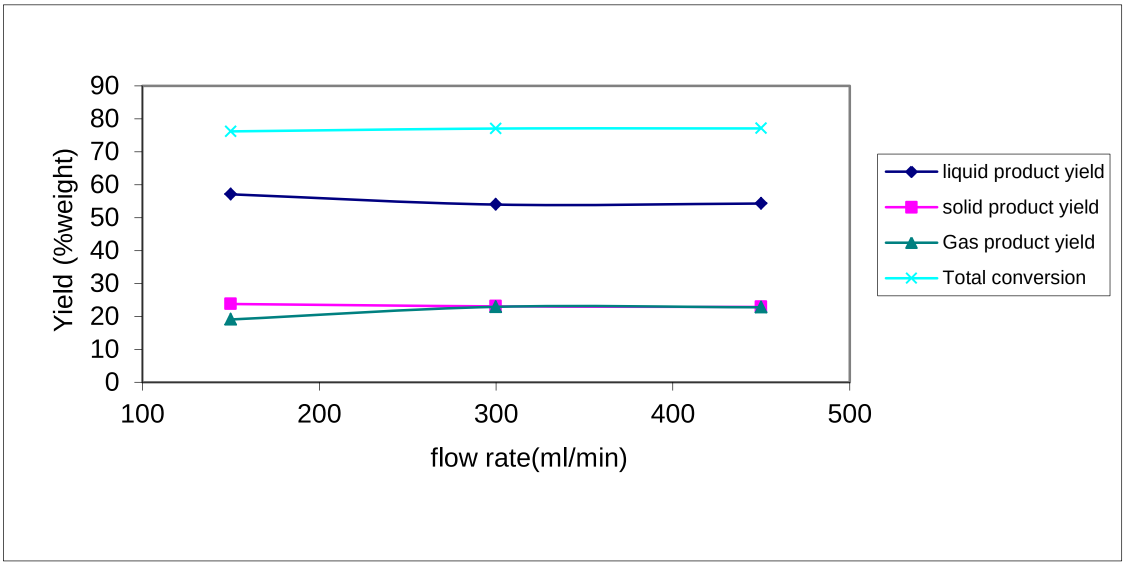


Figure 5.3 The effect of sweeping gas (nitrogen)flow rate on pyrolysis product yields

The results show that total conversion was 76.2% at 150 ml min^{-1}, and represented a very slight increase reaching to 77.1 at 450 ml min^{-1}. On the other hand, liquid product yield was 57.1% at 150 ml min^{-1}. Increasing the sweeping gas flow rate from 150 ml min^{-1} to 450 ml min^{-1} decreased the liquid product yield, but increased gas product yield. The highest increase in gas yield was observed at 450 ml min^{-1}. Solid product yield stayed almost constant at around 23%.

The residence time of the pyrolysis vapors in reactor is an important factor that determines the time available for vapor phase and vapor-solid phase reaction. Low nitrogen flow rate means higher vapor residence time since the pyrolysis vapors are removed lately from the hot reaction medium. This results in low liquid product yield since secondary reactions of vapors such as thermal cracking, repolimerization and recondensation take place. However, further increments of nitrogen flow rate caused a significant and continuous decrease in liquid product yield. Higher nitrogen flow rate decreases both the vapor residence time in reactor and the vapor residence time in condenser. This situation may interrupt the condensation allowing the pyrolysis vapors to escape the condersers as gaseous products (Açıkalın et al., 2012).

According to the results obtained in this part of work, the effect of increasing sweeping gas flow rate does not seem to be highly effective on the total conversion. Among the studied parameters, pyrolysis temperature can be assigned as the main determinative factor in pyrolsis conversion.

5.2 Experimental Design

The individual effects of parameters that were chosen in the first phase of the study were analyzed. In the second phase of the study, pyrolysis yields of apricot kernel were modelled by using Box-Behnken experimental design method. Temperature, reaction time and sweeping gas flowrate were the factors whose effects on total conversion, liquid product, gas product and solid product yields were studied in the ranges of 350-650^{o}C, 10-50 min. And 150-450 ml min^{-1}., respectively. In the second phase, to detect the alterations of the yields that were obtained by the simultaneous change of parameter values, experimental desing methods were carried out that were multivariate method of analysis.

The coded valued of factors were calculated from the original values with the help of the formula below as mentioned before in section 4:

X= [original value – midpoint value] / [interval value]

According to this formula, the relations between the coded and the original values were as given below:

$$x_1 = \frac{Temperature - 500}{150}$$

$$x_2 = \frac{Reaction\ time - 30}{20}$$

$$x_3 = \frac{Sweeping\ gas\ flowrate - 300}{150} \qquad (5.5)$$

The original values of each factor and their corresponding levels are shown in Table 5.5.

Table 5.5 The parameter values and their levels used for Box-Behnken design

DEGREE	T (°C)	RT (minute)	SGR (ml/min)
BOX – BEHNKEN DESIGN			
-1	350	10	150
0	500	30	300
+1	650	50	450

The levels related to the experiments and the results derived from the experiments which are carried out according to Box-Behnken design method are given in Table 5.6.

Table 5.6 The coded values for experimental design and the results for liquid, gas, solid product yields and total conversions

x_1 $x_2 x_3$	liquid (%)	gas (%)	solid (%)	TC (%)
1 1 0	48,6	34,3	17,1	82,9
1 -1 0	51,4	26,3	22,3	77,7
-1 1 0	48,5	21	30,5	69,5
-1 -1 0	48,6	21	30,4	69,6
1 0 1	47,2	33,4	19,4	80,6
1 0 -1	53,1	28,3	18,6	81,4
-1 0 1	52	18,1	29,9	70,1
-1 0 -1	47,6	23,5	28,9	71.1
0 1 1	48,2	29,4	22,4	77,6
0 1 -1	53,1	29,8	17,1	82,9
0 -1 1	55,7	26,7	17,6	82,4
0 -1 -1	54,5	25,8	19,7	80,3
0 0 0	54,5	22,6	22,9	77.1
0 0 0	54,2	22,8	23	77
0 0 0	53,6	23,2	23,2	76,8
0 0 0	53,5	24,1	22,4	77,6
0 0 0	54,1	22,7	23,2	76,8

5.3 Model Equation Development and Eligibility Check

The answers which derived from the experiments in the light of experimental design are identified as fuction of the factors. In order to create model equations, various polynomial models are used. These polinomals indicate how system answer are affected by parameter values being changed at the same time. Polynomial model that is used usually in designs giving response surface like Box-Benhken design is shown in equation 5.6.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j>i}^{k} \beta_{ii} x_i x_j \qquad (5.6)$$

Here, Y represent the system responce; β_0 is the constant value; β_i, β_{ij} are the each factor's coefficient; x_i, x_j are coded factors and k is factor number. If equation (5.6) is regulated for three factors, the equations below are arisen:

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 \qquad (5.7)$$

In the regression analysis which is used to calculate coefficient required for creating model, Design Expert [Design Expert Version 7.0.0, Stat-Ease] software was used. In terms of the polynominal statements mentioned above in the calculation of product yields, terms thet belong to the coefficients was removed from the model which do not provide 90% the materiality degree ($\alpha = 0,1$) which is the criteria within the scope of F-significance test for each coefficient. An extra calculation was not made, sinc Design Expert software implements this test for each coefficient and indicates terms that should be removed from the model.

In order to understand the convenience degree between the outcomes of experiments and polynomials that gained as model equations, sum of residuals and correlation coefficient were surveyed. The relation degree of sum of residuals ($\sum e$) to 0, correlation coefficient (R) to 1 has indicated the relation degree between the results of model equation obtained and experimental results. Furthermore, it is known that if the experimental design has a lot of parameters and levels, the correlation coefficient may not be sufficient by itself to check the fitted model. Thus, ANOVA analysis was also done in this work.

5.3.1 Models obtained with Box-Behnken design

5.3.1.1 Model equations for total conversion

Using experimental data in Table 5.6, after doing the regression analysis that gives coefficients of responce function and eliminating terms which do not fit the F-significance test, model equation developed for total conversion which was presented with equality (5.8).

$$Y_{TC}=76,86+5,2875x_1+0,3625x_2-0,625x_3+1,325x_1x_2+0,05x_1x_3-1,85x_2x_3-3,4675x_1^2+1,5325x_2^2+2,4075x_3^2 \quad (5.8)$$

Sum of the residual for total conversion model equation has been found out as 1,16, and correlation coefficient has been found out as 0,9759. The results of variance analysis are given in Table 5.7.

Table 5.7. Analysis of variance **(**ANOVA) for total conversion.

	SOURCE	**DEGREE OF FREEDOM (*v*)**	**SUM OF SQUARES(SS)**	**MEAN SQUARES (MS)**	**F RATIO**
APRICOT KERNEL	*MODEL*	9	329,29	36,59	31,54
	RESIDUAL	7	8, 12	1,16	
	TOTAL	16	337,4		

As a result of variance analysis, P values calculated by Design Expert software for total conversion model are smaller than 0,0001 value. Since P values are smaller than 0,01 model equation obtained has the condition of 99% confidence limit. It is decided that there is no need for any change in model equation as required of 95% confidence limit.

5.3.1.2 Model Equation for Liquid Product Yield

For liquid product yield model equation was given in Equation 5.9.

$$Y_L=53,98+0,45x_1-1,475x_2-0,65x_3-0,675x_1x_2-2,575x_1x_3-1,525x_2x_3-3,8025x_1^2-0,9025x_2^2-0,2025x_3^2 \qquad (5.9)$$

Sum of the residual for liquid product yield was obtained 0,92 and correlation coefficient was obtained as 0,9519. Variance analysis results are shown in Table 5.8.

Table 5.8 Analysis of variance **(**ANOVA) for liquid products

	SOURCE	**DEGREE OF FREEDOM (*v*)**	**SUM OF SQUARES (SS)**	**MEAN SQUARE (MS)**	**F VALUE**
APRICOT KERNEL	*MODEL*	9	126,98	14,11	15,39
	RESIDUAL	7	6, 42	0,92	
	TOTAL	16	133,4		

As a result of variance analysis, P values calculated by Design Expert software for liquid product yield model of apricot kernel shells are less than 0,0001 value. Because P value calculated for liquid product yield model is smaller than 0,01, it satisfies the conditions of 99% confidence limit. Thus, it is decided not to make a change in model equation.

5.3.1.3 Model equation for gas product yield

In the experiments carried out in compliance with experimental design, model equation obtained for solid product yields after acquired solid product yield values were exposed to regression analysis and after the terms that didn’t fit the F-significance test were eleminated, are given in Equation (5.9) for apricot kernels.

$$Y_G=23,08+4,8375x_1+1,8375x_2+0,025x_3+2x_1x_2+2,625x_1x_3-0,325x_2x_3+0,235x_1^2+2,335x_2^2+2,51x_3^2 \qquad (5.9)$$

Correlation coefficient has been found out as 0,9934 and sum of the residual for total conversion model equation has been found out as 0,30. Variance analysis results are shown in Table 5,9.

Table 5.9. Analysis of variance **(**ANOVA) for gas product yield

	SOURCE	**DEGREE OF FREEDOM (*v*)**	**SUM OF SQUARES (SS)**	**MEAN SQUARE (MS)**	**F VALUE**
APRICOT KERNEL	*MODEL*	9	311,51	34,61	116,46
	RESIDUAL	7	2, 08	0,3	
	TOTAL	16	313,6		

P values calculated calculated by Design Expert software for gas product yield models of apricot kernels are smaller than 0,0001 value. Confidence limit was found 99%. Thus, because of the demanded importance level is 95%, it is decided not to make a change in model equations.

5.3.1.4 Model equation for solid product yield

In the experiments carried out in compliance with experimental design, model equation enhanced for solid product yields after acquired solid product yield values were exposed to regression analysis and after the terms that didn't fit the F-significance test were eleminated, are given in Equation(5.10) for apricot kernels.

$$Y_S=22{,}94-5{,}2875x_1-0{,}3625x_2+0{,}625x_3-1{,}325x_1x_2-0{,}05x_1x_3+1{,}85x_2x_3+3{,}5675x_1^2-1{,}4325x_2^2-2{,}3075x_3^2 \qquad (5.10)$$

Correlation coefficient has been found out as 0,9780 and sum of the residual for total conversion model equation has been found out as 1,06. Variance analysis results are hown in Table 5.10.

Table 5.10. Analysis of variance **(**ANOVA) for solid product yield

	SOURCE	DEGREE OF FREEDOM (*v*)	SUM OF SQUARES (S S)	MEAN SQUARE (MS)	F VALUE
APRICOT KERNEL	*MODEL*	9	328.98	36,55	34,58
	RESIDUAL	7	7, 40	1,06	
	TOTAL	16	336,38		

As a result of variance analysis, P values calculated by Design Expert software for solid product yield model of apricot kernel shell are smaller than 0,0001 value. Because P value calculated for liquid product yield model is smaller than 0,01, it satisfies the conditions of 99% confidence limit. Because the demanded confidence limit is 95%, it is decided not to make a change in model equation.

5.3.1.5. The Interpretation of Model Equations

The models obtained show that temperature ($x_{1)}$ has the strongest effect on total conversion and pyrolysis product yields since the β coefficient of x_1 is larger than the coefficient s of the other investigated factors. Positive sign of this coefficient indicates that there is a direct relation between temperature and total conversion, liquid and gas product yields; in other words, total conversion, liquid and gas product yields will increase with increasing temperature. However, solid product yield will decrease with increasing temperature as expected. The negative sign of this factor indicates an inversely proportional relatioship between temperature and solid product yield.

5.4 Product Analysis

5.4.1 Solid Product Analysis

5.4.1.1 SEM analysis

The microstructure of solid products obtained at 350, 500 and 650^{o}C have been observed by Scanning Electron Microscopy (SEM). The micrographs were obtained by using Jeol JSM-6390LV model device in Marmara University, Department of Metallurgical and Materials Engineering Laboratory and given in Figure 5.4.

In figure 5.4, the micrographs of solid products which obtained at 30 min reaction time, 300 ml/min sweeping gas flow rate, 40°C/min heating rate and 350, 500, 650 °C temperatures, respectively. It can be seen that the externa surface structure of solid products were strongly affected by the applied pyrolsis temperature. The solid product obtained at 350^{o}C had an undulating surface with some rudimentary pores. The product obtained at 500^{o}C had a more irregular and distorted surface in contrast to the product obtained at lower temperature. There were some broken particles on the surface, and the pore forming was clearly observed. The surface of the product obtained at 650^{o}C was found to be the most irregular and distorted surface with many pores on itself.

According to the micrographs, it can be said that the porosity of the solid product showed an increasing trend as the applied pyrolysis temperature increased.

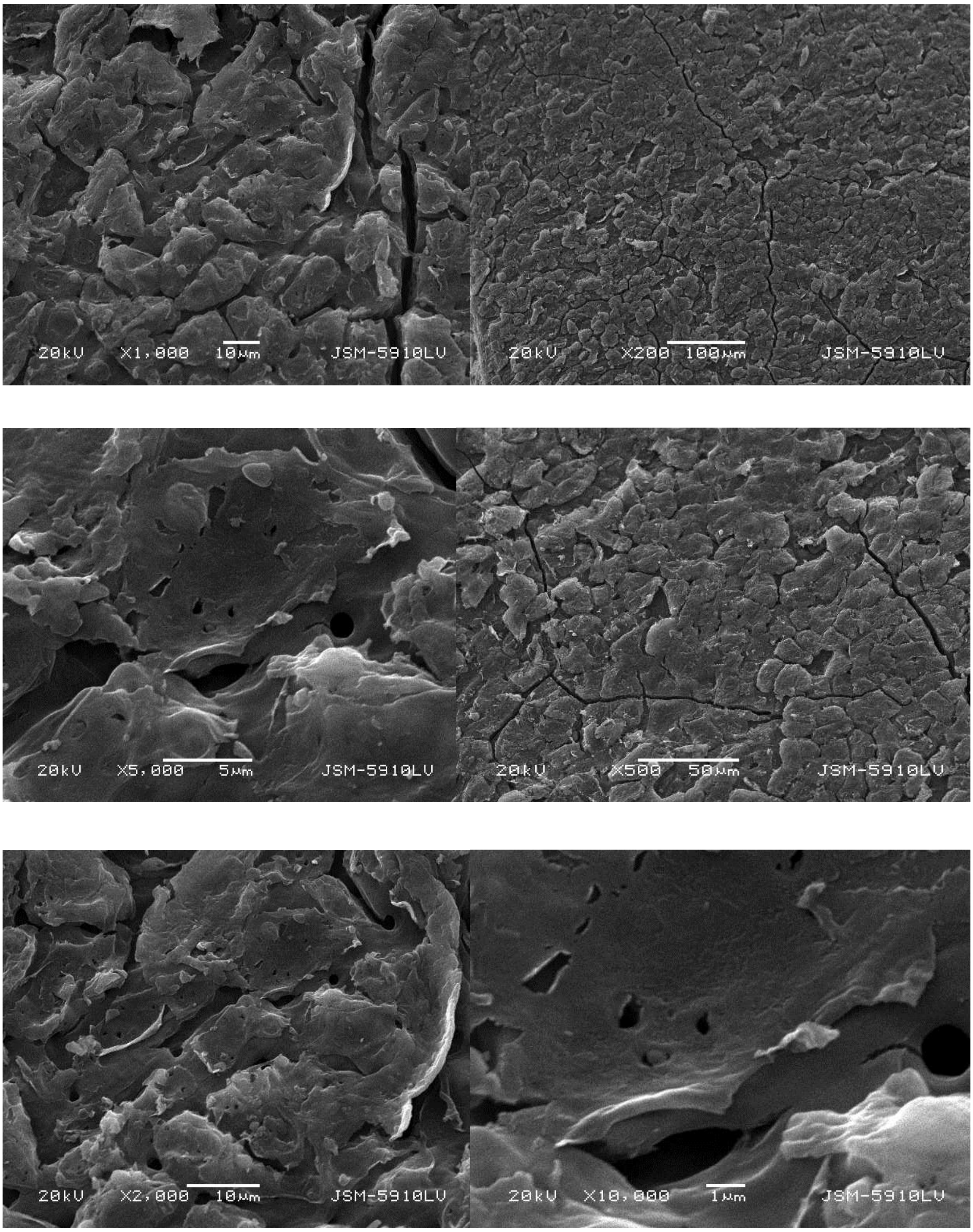


Figure 5.4 SEM analysis of solid products at 350, 500 and 650^{o} temperature, respectively.

5.4.1.2. FTIR Analysis

The FTIR spectra of solid products obtained at 30 min reaction time, 250 ml/min sweeping gas flow rate and 40°C/min heating rate and three different pyrolysis temperatures were given in Figures 5.5-5.7. When the spectra were compared with the spectrum of original apricot kernels (Figure 4.1) it was noticed that some of peaks availablable in apricot kernel disappeared or appeared at low intensities. This indicated that some of functional groups present in apricot kernel were removed (or partially removed) from the structure as pyrolysis temperature increased. On the solid product spectra obtained at different temperatures, the peak observed at about 3050 cm^{-1} band was due to O-H stretching vibrations in hydroxyl groups, and it was observed nearly at the same intensity for spectra of solid products obtained at 350 and 500^{o}C temperatures. The intensity of the peaks observed in apricot kernel shell at 2969 derived from the asymmetrical and symmetrical C-H voltage in the methylene group were considerably low in solid products, indicating that it had a less aliphatic content when the solid product was compared to apricot kernel. At about 1730 cm^{-1} wave long peak arises from C=O in carbonyl groups and it signifies the presence of groups such as acetyl derivatives and aldehyde groups. The peak that is observed at 1583 cm^{-1} but, that isn't available in the apricot kernel, can be connected to the disintegration of C=C olefinic links in apricot kernel during pyrolysis. The peaks apperared at around 1456 and 1385 cm^{-1} were caused by methylene symmetrical C-H stretching. The intensity of these peaks were observable at low temperatures but they became considerably less observable at high temperature. This indicated a decrease in aliphaticity of solid product as the applied pyrolysis temperature increased.

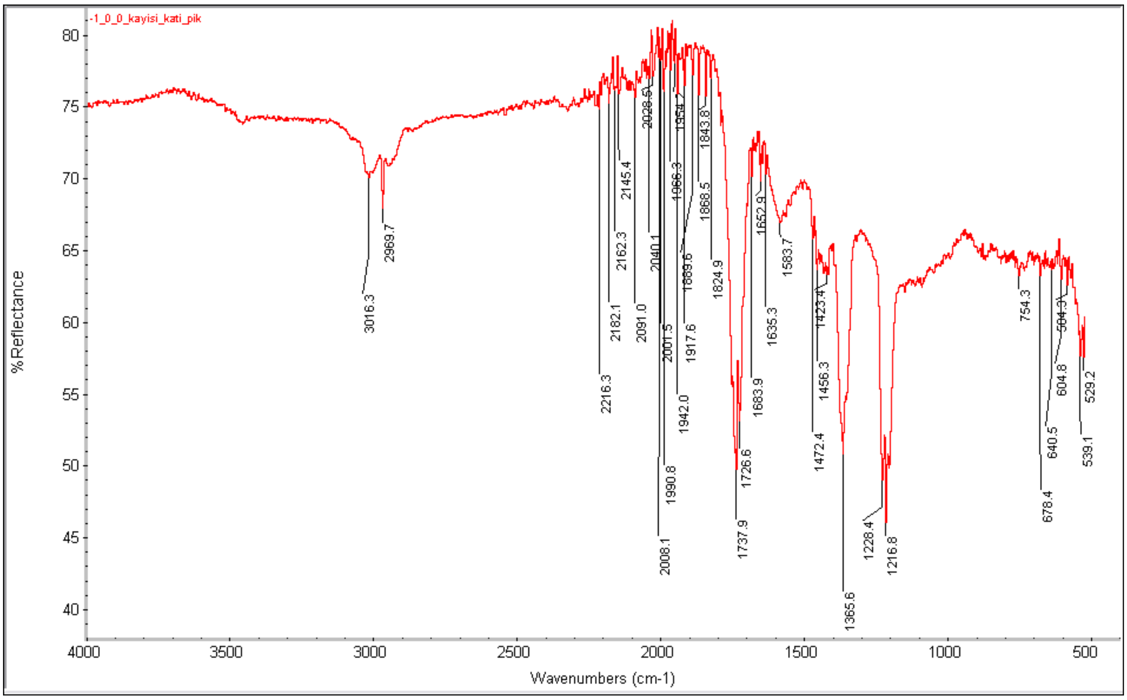


Figure 5.5 FTIR spectrum of apricot kernel’s solid pyrolysis product at 350°C

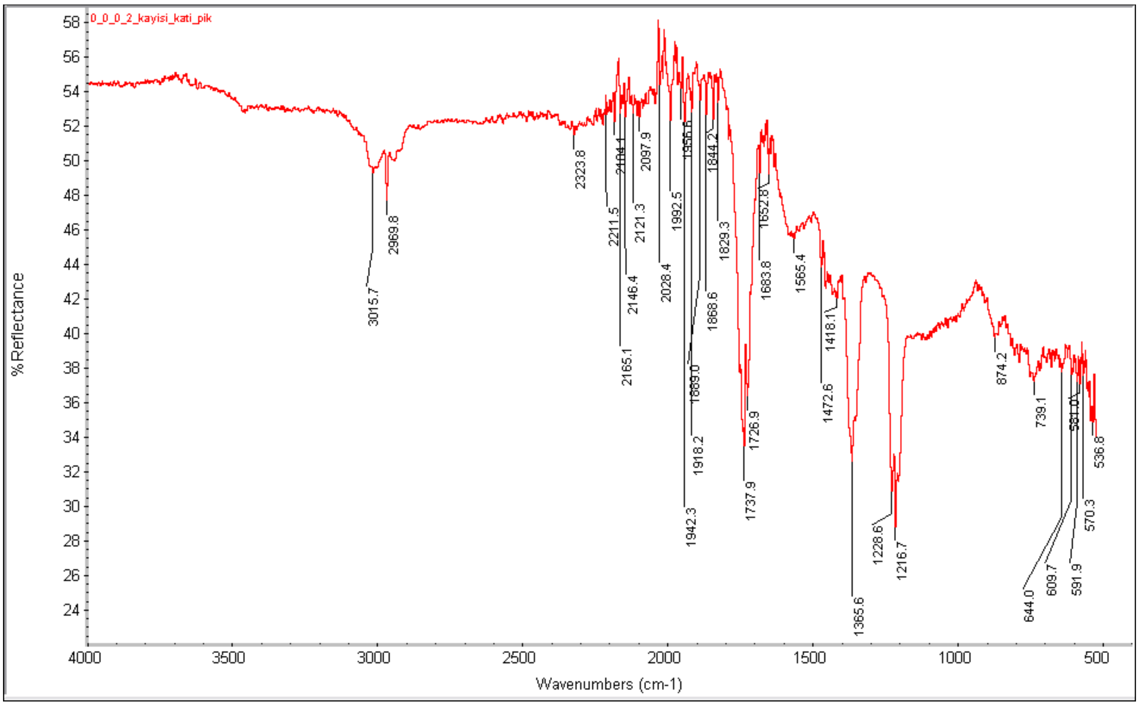


Figure 5.6 FTIR spectrum of apricot kernel’s solid pyrolysis product at 500°C

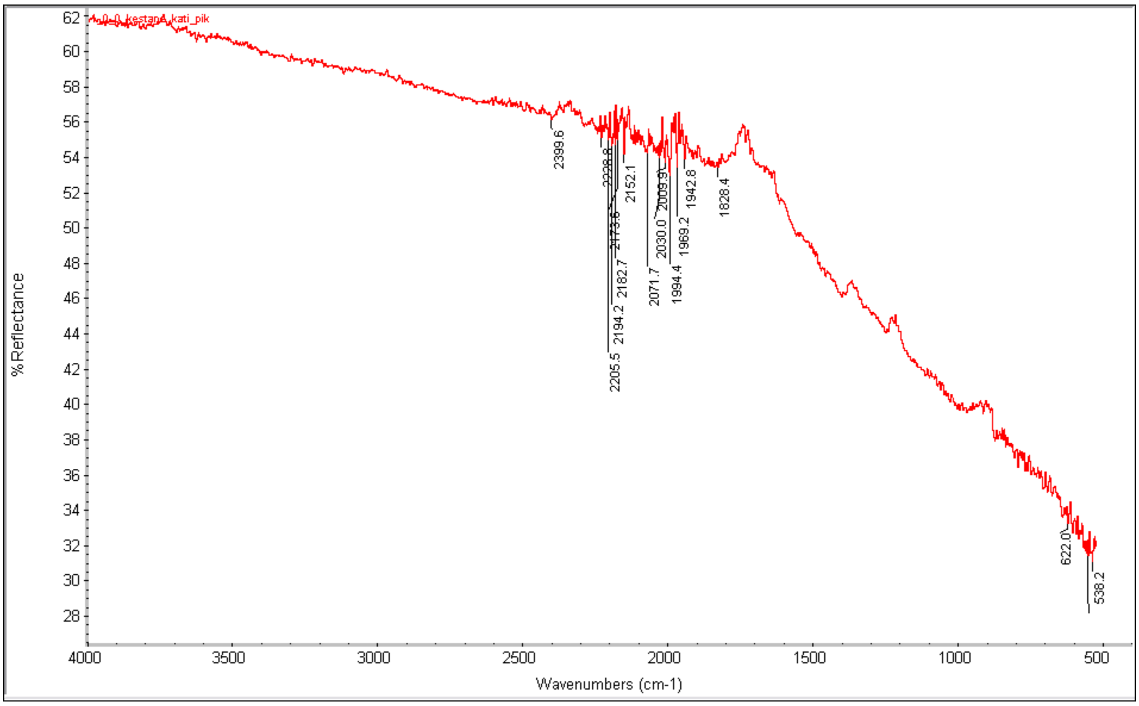


Figure 5.7 FTIR spectrum of apricot kernel's solid pyrolysis product at 650°C

5.4.2 Liquid product analysis

5.4.2.1 FTIR analysis

FTIR spectra of liquid products obtained at 350, 500 and 650^{o}C pyrolysis temperatures, respectively were given in Figures 5.8-5.10. It can be said that, the spectra were similar to the spectrum of apricot kernel indicating that most of the functional groups available in apricot kernel were also present in liquid products but at different intensities. It was also clear that the liquid product spectra obtained at different temperatures were identical to each othar. The liquid product cosiste of same types of chemical compounds independently from th pyrolysis temperature. The liquid product was mainly formed by the condensation of volatiles originating from cellulose and hemicellulose which decompose completely at low temperatures around 350^{o}C. The peak around 3375-3330 cm^{-1} was due to the O-H stretching vibrations, and can be assigned to hydroxyl groups (water, alcohols, phenols or carboxylic acids). The peak at 2969 cm^{-1} was ascribed to symmetrical and asymmetrical C-H stretching vibrations of aliphatic $-CH_3$ and $-CH_2$- groups and indicated the presence of alkane groups. The intensive C=O stretching vibrations with transmittance at 1737-1723 cm^{-1} show the abundant presence of ketones and aldehydes. The peak at 1652-1611 cm^{-1} represents C=C $^{st-}$1retching vibrations indicative of alkanes and aromatics (Yadav, 2005). The peak observed at 1513 cm^{-1} can be ascribed to skeletal strech of aromatic compounds. The peak at 1365 cm^{-1} was valuable for the detection of methyl groups, and was due to the presence of alkane groups. The peaks between 1220 and 1020 cm^{-1} were caused by C-O stretching and O-H deformation vibrations and pointed out the presence of alcohols, phenols, ethers and esters (Şensöz and Angın,2008b).

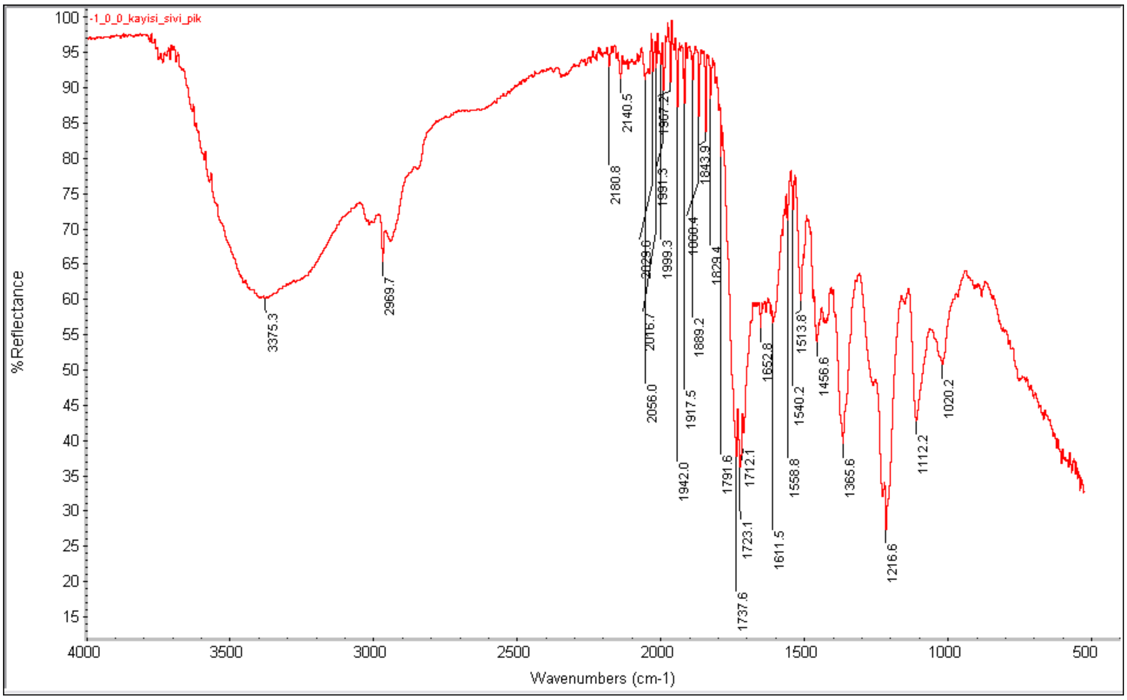


Figure 5.8 FTIR spectrum of apricot kernel’s liquid pyrolysis product at 350°C

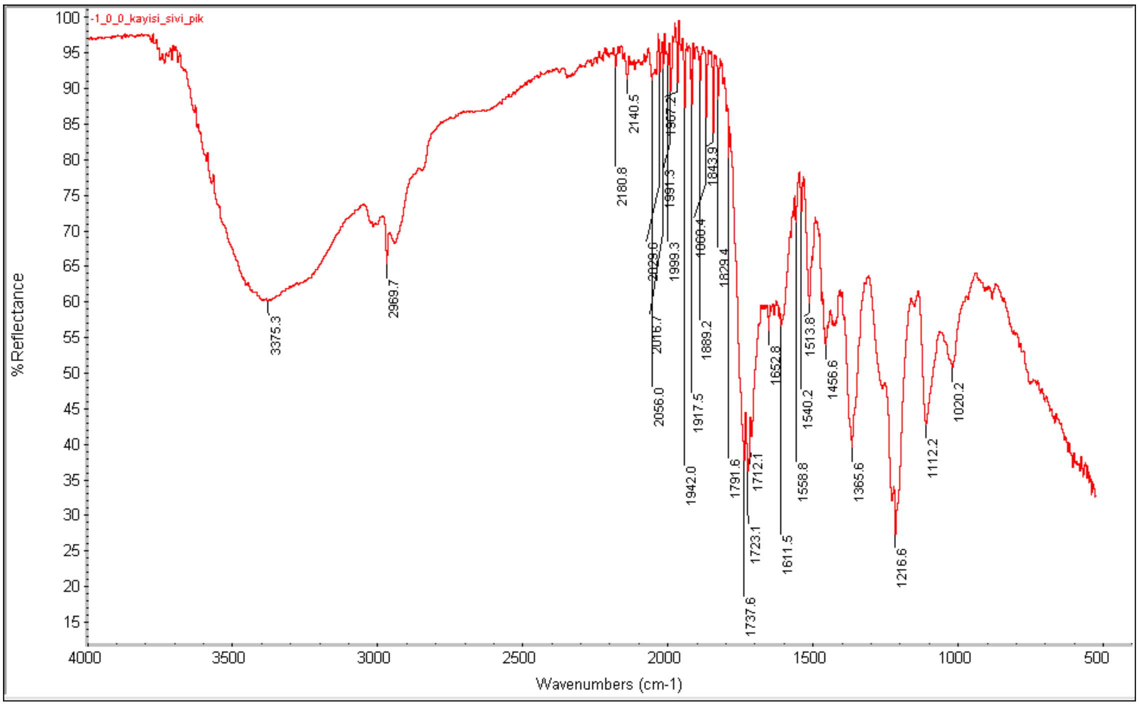


Figure 5.9 FTIR spectrum of apricot kernel's liquid pyrolysis product at 500°C

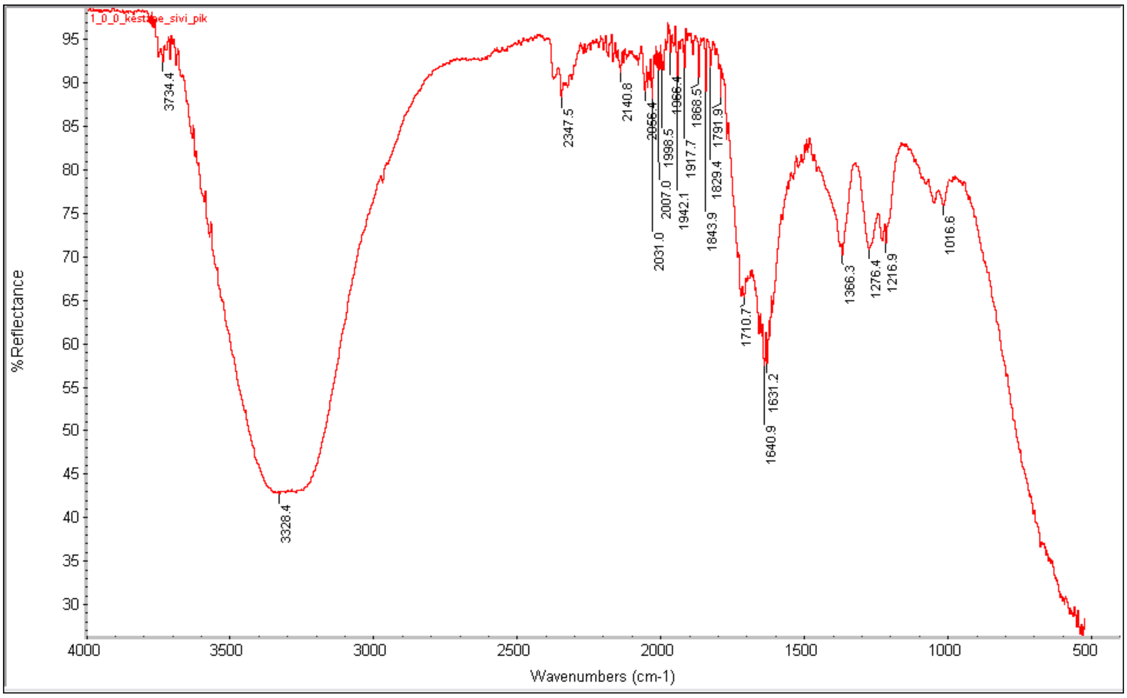


Figure 5.10 FTIR spectrum of apricot kernel's liquid pyrolysis product at 650°C

6. CONCLUSIONS

In the studies that the effects of chosen parameters on apricot kernels pyrolysis product yields were analyzed and the results below were obtained:

- In the experiments where the temperature carried out between 350-650°C at 30 min reaction time, 300 ml/min sweeping gas flow rate and 40°C/min heating rate. It was observed that total conversion for this biomass waste material increased with temperature, the liquid product yield was not effected, gas product yield increased for this biomass waste material with increasing temperature, and the solid product yield decreased with increasing temperature.
- In the experiments where the temperature was fixed at 500°C, the sweeping gas flow rate as 300 ml/min, the heating rate as 40°C/min, and the effects of reaction time on pyrolysis product yields were analyzed. It was observed that gas product yield was not very changed with the reaction time and solid product yield decreased with the reaction time. Liquid product yield reached the maximum value at 50 min reaction time for the this biomass waste material, and total conversion yields increased with increasing the reaction time.
- In the experiments that the effects of sweeping gas flow rate on the pyrolysis product yields were analyzed studying at 150-450 ml/min range and the temperature, reaction time, heating rate values was fixed at 500ºC, 30 min, 40ºC/min respectively. It was determined that total conversion and gas product yields increased with increasing sweeping gas flow rate. Solid product yields decreased when sweeping gas flow rate increased. At 150 ml/min gas flow rate liquid product yields reached the maximum values after that when flow rate increased to 300 ml/min, liquid product yields decreased after that liquid product yields increased with increasing of sweeping gas flow rate.
- Total conversion, liquid, gas and solid product yield models were analyzed statistically with Variance Analysis and it was indicated that all the models that were derived, provided the 95% significance level.
- SEM micrographs of solid products that were obtained in the pyrolysis experiments carried out at 30 min reaction time, 300 ml/min sweeping gas flow rate, 40°C heating rate and different reaction temperatures (350, 500, 650°C),

showed that the solid product obtained, took a more porous shape as long as the pyrolysis temperature was increased.

- FTIR analysis of the liquid products obtained at 500°C reaction temperature, 30 min reaction time, 300 ml/min sweeping gas flow rate, and 40°C/min heating rate, were carried out. When spectrums of the liquid products were compared to original sample, most of the peaks in original sample were also present in the liquid product, unlike the solid products. When FTIR spectrum of the liquid product acquired by apricot kernel was compared to apricot kernel, it was observed that there was an increase in the intensity of the peaks (1737 cm^{-1}) derived from aldehyde and ketone content in particular. On the other hand, the peaks (3375 cm^{-1}, 1220-1020 cm^{-1}) derived from alcohol, phenol, ester, ether content were also present in the liquid product like they were in the kernels.
- Calorific values of the liquid products obtained at 500°C reaction temperature, 30 min reaction time, 300 ml/min sweeping gas flow rate and 40°C/min heating rate was calculated and determined as 4896 kcal/kg. However, this value is approximately half of the calorific values of petroleum product fuels.

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Öğrenim Durumu

Degree	Dept/Program	University/High School	Graduate Year
High School	NATURAL AND APPLIED SCIENCES	SAKIP SABANCI ANATOLIAN HIGH SCHOOL	2003
University	CHEMICAL ENGINEERING	UNIVERSITY OF KOCAELI	2010

Job Experiences

Year	Firm/Company	Title
2012-	JMS INTERNATIONAL TRANSPORT	IMPORT CUSTOMER REPRESENTATIVE