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Optimizing Factors Affecting Oil Yield Derived from Pyrolysis of Cypress Pruning Residues Using Response Surface Methodology

Ali Doorandish and Ahmad Ghazanfari Moghaddam
Department of Mechanic of Biosystems, Shahid Bahonar University of Kerman, Kerman, Iran

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Corresponding Author:
Ali Doorandish
Department of Mechanic of Biosystems, Shahid Bahonar University of Kerman, Kerman, Iran

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Abstract: Cypress pruning residues have the potential to be converted to bio-oils using a pyrolysis process. In this research, cypress-pruning residues including ground particles of stems and leaves were separately pyrolysed to produce pyrolysis oil. A fixed-platform reactor equipped with a condenser was used for deriving pyrolysis oil from cypress pruning residues. The effect of pyrolysis and condensing temperatures on the yield of bio-oils were investigated and optimized using the RSM. The investigated reactor temperature ranged from 350-60°C and the condensing temperature ranged from-5-20°C. The results indicated that the thermal values of the bio-oil obtained from stem and leaf samples were 22.32 and 24.02 MJ kg^{-1}, respectively which showed an increase of about 30% compared to the thermal values of their corresponding raw materials. The optimum operating reactor temperature was 523°C for the stem particles and 494°C for the leaves particles. The optimum condensing temperature for both leaves and stem particles was -12°C. At the optimum conditions, the yield of pyrolysis oil was (33% w/w) for the stem particles and (14% w/w) for the leaves particles.

INTRODUCTION

Increase in daily consumption, rapid reduction of resources, political dependency and environmental concerns regarding the usage of fossil fuels have led many countries to reduce their dependency on fossil fuels and investigate the possible use of renewable, sustainable and clean energy sources. Among the alternative sources of energy, biomass has gained considerable attention. Biomass fuels are renewable and contain less amounts of sulfur and they are lead free, thus causing less environmental pollution. It is predicted that by the year 2050 biomass will supply about 38% of the world's energy[1].

Pyrolysis is a promising method for deriving various fuels from biomass. In this process, biomass is heated at a temperature range of 350-900°C in the absence of oxygen wherein, biomass is decomposed and converted into char and gases. The emitted gases can be cooled and converted topyrolysis oils which can be used as a source of liquid type energy. The extracted pyrolysis oils are usually dark brown, free-flowing liquids with a distinctive smoky odor. These oils are complicated biochemical compounds that contain various types of organic acids, aldehydes, alcohols, sugars, esters and aromatic compounds[2].

Several factors such as reactor temperature, heating rate, type and flow rate of carrier gas and particle size of pyrolysis material play an important role in the amount pyrolysis yields. In the pyrolysis of rice straw, it was shown that with increasing the reactor temperature from 300-600°C, the amount of obtained bio-oil increased from 32-45%[3]. In the pyrolysis of coffee waste amount of produced oil was 45% when reactor temperature was 450°C and bio-oil yield increased by11% when reactor temperature raised to 500°C and the oil amount decreased to 55% by increasing temperature up to 550°C[4]. In another research on pyrolysis ofcassavastem and roots it was indicated that temperature had significant effect of the yield and the optimum temperature for stem pyrolysis was 475°C and for root pyrolysis was 469°C[5].

Heating rate is another factor that influence the yield of a pyrolysis process. In a research on the pyrolysis of fennel (*Ferula orientalis* L.) stems performed at 350°C with three heating rates of 15, 30 and 50°C, char yields for the respected rates were 39, 41 and 42%, indicating an increase in yield with increase in heating rate[6]. In the pyrolysis of olive processing waste, the yield of bio-char at 480°C and at heating rates of 25, 35 and 45°C/min was 34.5, 31.3 and 26.8%, respectively[7]. Also, in the production of pyrolysis oil from linseed by fast pyrolysis, the highest oil yield was achieved at a heating rate of 30°C min^{-1}. Oil yield in these conditions was 57[8].

The size of biomass particles is also a factor that play a major role in the production of pyrolysis products. Generally, particle size affects the mass and heat transfer phenomenon during a pyrolysis process and it alters the secondary chemical reactions and decompositions that take place within the biomass particles. In canola seed pyrolysis an increase in the average diameter of the particles from 0.2-1.8 mm caused an increase in the yield of oil produced but the oil yield deceased when particle size exceeded 1.8 mm[9]. Also, in the pyrolysis of fennel stem at 500°C and the heating rate of 50°C min^{-1}, the amount of oil was reduced by increasing the average diameter of the particle from 0.2-0.8 mm[6]. In general, finer biomass particles are preferred in a pyrolysis process.

Cypress (*Cupressus sempervirens* L.) is an evergreen coniferous tree that are resistant to drought and grow in most parts of the world. The thermal value of its wood is about 18 MJ kg^{-1} while the oil obtained from pyrolysis has a thermal value of 20-22 MJ kg^{-1}[10]. The oil extracted from the woody part of the cypress trees contain different biochemical compounds including α-pinene, δ-3-carene, limonene and α-terpinolene with general chemical formula of $C_{10}H_{16}$[11, 12]. These compounds are combustible and can be used as a source of bioenergy. The residues of annual pruning this tree has the potential to be converted to higher thermal value biofuels through pyrolysis process. However, the effects of various factors on pyrolysis of these materials need to be investigated and optimized.

In various pyrolysis investigations, the effects of operational parameters on the yield of different components are investigated and the factors levels are optimized to maximize the yields. The Response Surface Method (RSM) is frequently used to examine the effect of several independent variables on the dependent variable. This method consist of a set of mathematical and statistical techniques that initially helps in selecting a design of experiment and a combination of the dependent variables affecting the dependent variables. The method is also include developing appropriate mathematical relationship between factors and responses and optimizing the considered factors to maximize or minimize the responses[13].

The main purpose of this research was to use the residues from cypress pruning as a source of pyrolysi soil. In this investigation, RSM was used to study the effect of different production factors on the amount of bio-oil yield and the bio-oil yields were modeled as functions of reactor and condenser temperatures. Then, the reactor and condenser temperatures were optimized to maximize the yield of pyrolysis oils.

MATERIALS AND METHODS

Evaluation of raw materials: The cypress pruning collected for the experiments were divided into two groups of leaves and stems residues. The samples were kept in the laboratory for 2 weeks to dry and reach an equilibrium moisture content. Then, 100 g of each sample was placed in oven dried at 105°C for 24 h to determine their moisture content. Since, the heating value is an important characteristics of any material to be used as fuel, the High Heating Value (HHV) and Low Heating Value (LHV) for the raw materials and pyrolysis products were determined using Eq. 2 and 3, respectively[14]:

$$\begin{aligned}HHV = 0.3491C+1.1783+0.1005S-\\ 0.1034O-0.0151N-0.0211A\end{aligned} \quad (1)$$

$$LHV = HHV-0.2182H \quad (2)$$

In these equations C, H, N, O, S and A are the percentage of Carbon, Hydrogen, Nitrogen, Oxygen Sulfur and ash content of the material, respectively. The percentage of each of these elements were determined by ultimate analysis of the samples using a CHNOS elemental analyzer. The amount of ash in each sample was determined by heating them in a muffle furnace at550°C for 5 h and determining the mass of solid portion remained in the furnace. Then, the percentage of oxygen for each sample was calculated by:

$$O = 100(\%)-(C+H+A+N+S) \quad (3)$$

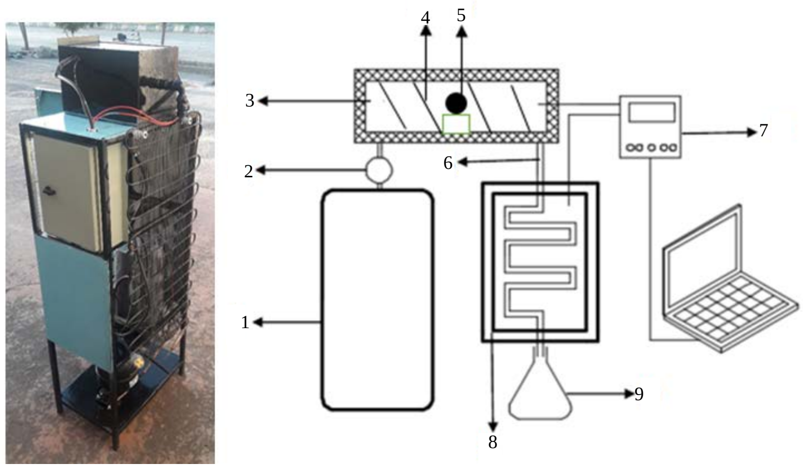

Fig. 1(a-b): The pyrolysis setup; a) picture; b) schematic drawing: 1; Carrier gas cylinder, 2; gas flow valve, 3; reactor, 4; heating elements, 5; sample holder, 6; emitted gases pipe, 7; control and monitoring board, 8; condenser, 9; pyrolysis oil container

Thermogravimetric analysis (TG) is a well established method for obtaining weight loss to study biomass thermal decomposition characteristics, evolved products during pyrolysis. Thus, thermogravimeteric tests were performed on stems and leaves samples to determine their thermal decomposition characteristics using athermogravimetry analyzer (PCLuxx409, NETZSCH, Germany). For each test, 25 mg of each samples were heated at temperatures ranging from 25-900°C with a heating rate of 10°C per minute and nitrogen gas was used as the carrier gas with a flow rate of 100 mL min^{-1}. In thermogravimetric tests, each time 25 mg of a sample was placed inside the analyzer and during the test, the weight losses at various temperatures were recorded overtime and the resulted charts were analyzed.

Pyrolysis experimental apparatus: For pyrolysis experiments, a pyrolysis system consisting of a fixed-platform reactor, a cooling system and temperature control and monitoring system was designed and built. The reactor of this system was a galvanized iron pipe with an internal diameter of 7 cm, a length of 30 cm with a thickness of 3 mm. Four spiral parallel 1000 wheating elements were used to heat the samples with different heating rates. The emitted gases were passed through a condenser that was made of aspiral copper pipe. The condenser was cooled by the flow of R134a refrigerant. The temperatures around the condenser and inside the reactor were monitored using K-type thermocouples connected to a control board. A schematic diagram of the system and a picture of it are shown in Fig. 1.

Conducting pyrolysis tests: Response Surface Methodology (RSM) based on the Central Composite Design (CCD) was used to evaluate the effect of reactor and condenser temperature on the yield of pyrolysis oil. Based on thermogravimeteric tests and preliminary studies, a temperature range of 350-600°C was used for the reactor and the surrounding of the condenser temperature was selected from -20 to -5°C. The number of experiments and their operational conditions required for this investigation were generated by Design Expert software (Table 2).

After specifying the operational conditions needed for the experiments, 100 g of each sample were placed inside the reactor and were heated at constant rate of 50°C min^{-1}. After reaching the desired temperature, the samples were kept at that temperature for 30 min to ensure complete decomposition of the raw material. Throughout the experiments, the emitted gases were passed through the condenser and the generated pyrolysis oil were collected. Then, the char deposited in the reactor was collected and weighed and the mass of exhaust gas from the reactor, before entering the condenser was estimated by subtracting the mass of char from the mass of the mass of sample inside the reactor. In all of these experiments, CO_2 gas was the carrier gas with a flow rate of 100 mL min^{-1}. The collected pyrolysis oil was weighed and the yield for each samples was calculated. Also, elemental analysis was performed on the collected pyrolysis oils and their thermal values were determined using (Eq. 1 and 2):

Optimization operational conditions: In RSM approach for determining the optimum values for independent variables, a second order polynomial should be used to state the response variable y as a function of the independent variables x. The general form of quadratic polynomial function is[13]:

$$y = \beta_0 + \sum_{j=i+1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i}^{k} \beta_{ij} x_i x_j \quad (4)$$

Where:

β_{ij} = The regression coefficients that are determined by least square procedure
k = The number of independent variables

The optimum values of the dependent variables were determined by taking the first partial derivatives of developed regression model and equating them to zero, i.e:

$$\frac{\delta y}{\delta x_1} = b_1 + 2b_{11}x_1 + b_{12}x_2 = 0 \quad (5)$$

Where:

x_1 = The reactor temperature
x_2 = The temperature of the surroundings of the condenser

Then, the optimum values are found by solving the resulting Eq. 5 simultaneously. In this investigation, modeling and optimization calculations were done using design expert software.

RESULTS AND DISCUSSION

Material analysis: The thermogravimetric curves for pyrolysis cypress residues at the heating rate of 10°C min^{-1} are presented in Fig. 2. Three stages of decompositions were identified in this graph. The first stage (3.26% weight loss) was attributed to moisture evaporation highly volatile compounds starting from about n 50°C and ending around 130°C. In this temperature range, the stem and leaf samples are lost %5 and 4% of its mass, respectively. The second stage is main weight loss between 180 and 550°C with a sharp decrease in the weight of cypress residues and this stage is usually associated with the hemicellulose, cellulose and lignin decomposition. The thermal decomposition temperature of hemicellu loses is 225-350, 325-375°C for cellulose and 250-500°C for lignin[15]. At this stage, the stem and leaf samples are lost 45 and 43% of its mass, respectively.

The third stage is attributed with formation of char, which is mainly made of carbon. At this stage, the rate of mass change decreases and mass samples continue to decrease up to 780°C. At the end of this stage, the char deposited for the stem residues is around 22% and for leaves residues is around 28% of their initial masses, indicating there are more carbon in the leaves than to the stems of cypress. The graph also indicates that both stem and leaf samples have the same thermal behavior and the similar temperature range can be considered for them for pyrolysis decomposition.

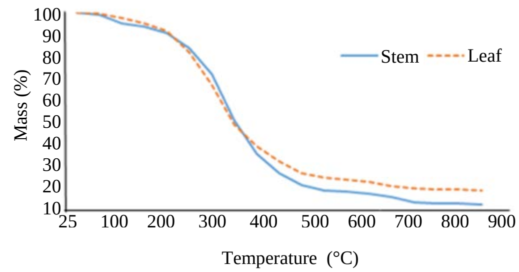

Fig. 2: The Thermogravimetric (TG) curve for stem and leaves of cypress pruning

The results of ultimate analysis of leaf and stem are shown in Table 1. This table shows that the amount of carbon and hydrogen elements in the leaf is higher than the stem samples. Thus, it is expected that the thermal value of the leaf sample to be higher than stem sample. Also in leaf samples, nitrogen and sulfur elements are more than stem samples, shows that the pollution's from direct burning of leaf samples should be more than stem samples, since, the oxides of these two elements are pollutants. The thermal values for raw samples were calculated using (Eq. 1 and 2) and they are listed in the last two rows ofTable1. The thermal value of raw stem and leaf samples is 17.08 and 18.77 MJ kg^{-1}, respectively. The results of ultimate analysis of extracted oils (Table 1) show that the oil obtained from both samples has less ash, nitrogen and sulfur but more carbon and hydrogen than the raw materials. Therefore, pyrolysis oils have less pollution potential with a higher thermal value than raw material. Oils obtained from stem and leaf samples have a thermal value of 22.32 and 27.85 MJ kg^{-1}, respectively. Although, these values have increased in comparison to the original raw materials, these oils have less thermal value than usual vegetable oils. For example, the thermal value of pure linoleic acid with the chemical formula $C_{18}H_{32}O_2$ which forms about 60% of sunflower oil is equal to 39.21 MJ kg^{-1}. The higher thermal values of common vegetable oils is due to the lack of oxygen and thus higher percentage of carbon and hydrogen. On the other hand, the pyrolysis oils contain considerable amount various compounds containing oxygen as well as the presence of other impurities in these oils which contributes to their lower heating values[5].

Oil yield: The experimental matrix for investigating the effects of the reactor and condenser temperatures on pyrolysis oil that was developed by the Central Composite Design (CCD) is shown in Table 2. The percentage of the resulting oils for both stems and leaves sample are presented in this table. The highest amount of pyrolysis

Table 1: Ultimate analysis and thermal values for stem and leaves of cypress pruning

	Stem		Leaf		
Materials	Raw	Bio-oil	Raw	Bio-oil	Linoleic acid
Ash (%)	5.7	1.3	6.3	1.7	0
C (%)	45.1	50.6	46.1	58.2	77.1
H (%)	4.9	7.4	5.5	6.1	11.4
N (%)	1.8	0.6	2.2	0.4	0
O (%)	44.3	40.7	42.1	33.4	11.4
S (%)	0.4	0.4	0.4	0.2	0
HHV (MJ kg^{-1})	17.08	22.32	18.37	24.02	39.21
LHV (MJ kg^{-1})	16.01	20.70	17.16	22.69	36.72

Table 2: Comparison ofoil yield (%) obtained from experiments and predictions by models

Factors/bio-oil yield (%)						
			Stem		Leaf	
Run	1	2	Experimental	Predict	Experimental	Predict
1	475	-12	31.3	31.7	12.8	13.8
2	652	-12	29.2	26.4	10.1	8.6
3	298	-12	14.8	12.7	6.5	5.6
4	475	-2	14.6	11.3	5.3	4.1
5	475	-12	30.7	31.7	13.7	13.8
6	600	-5	18.4	20.5	5.9	6.8
7	350	-20	7.6	7.9	2.2	2.6
8	600	-20	14.5	17.6	2.9	4.7
9	475	-12	32.3	31.7	13.4	13.8
10	475	-23	8.9	7.2	2.3	1.1
11	475	-12	31.9	31.7	13.8	13.8
12	475	-12	32.7	31.7	13.6	13.8
13	350	-5	6.8	10.8	3.3	4.7

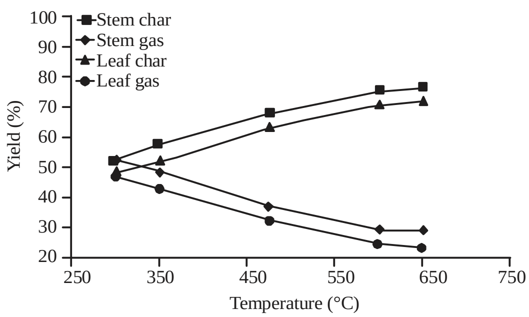

Fig. 3: The effect of temperature on the yield of char and gas yield for stem and leaves

oil, 32.3% for stems and 13.7% for leaves were obtained with a reactor temperature of 475°C and a condenser surroundings of -12°C. Minimum yield occurs at two treatments, 350°C for reactor and -5°C for condenser, 350°C for reactor and -20°C for condenser, indicating that 350°C is a low temperature for pyrolysis of cypress residues. At 475°C and -23°C the yield is also low, indicating that -23°C is very low for condenser surrounding.

Figure 3 shows the yield graph of the char and the exhaust gas in the reactor at different temperatures. In the stem sample. Char production decreased with increase in reactor temperature but the amount of exhaust gas from the reactor increased. The produced amount of char decreased from 52-29% for stems and from 48% to 23.7 for the leaves% with increase in reactor temperature from 300-650°C. Reduction of char is due to the further decomposition of solids with increasing temperature and causing increase in the percentage of produced gas. The figure indicates that the amount of char produced by the leaves residues is higher than the stem which is mainly due to higher percentage of carbon in the leaf (Fig. 3).

Modeling for pyrolysis oil yield: A summary of the ANOVA tests performed for evaluating the coefficients of the quadratic model for leaves and stem samples are presented in Table 3. In this table, the p-value for each of the terms of the equations are presented. Terms with a $p>0.05$ are not significant and should be eliminated from the equations. Based on this table in models for both stem and leaf samples, p-value for first-degree terms and second degree terms of reactor temperature and condenser temperature are significant. However, for the interaction term the effect between reactor temperature and condenser temperature was not significant. Based on these interpretations, the following second-degree polynomials were used to

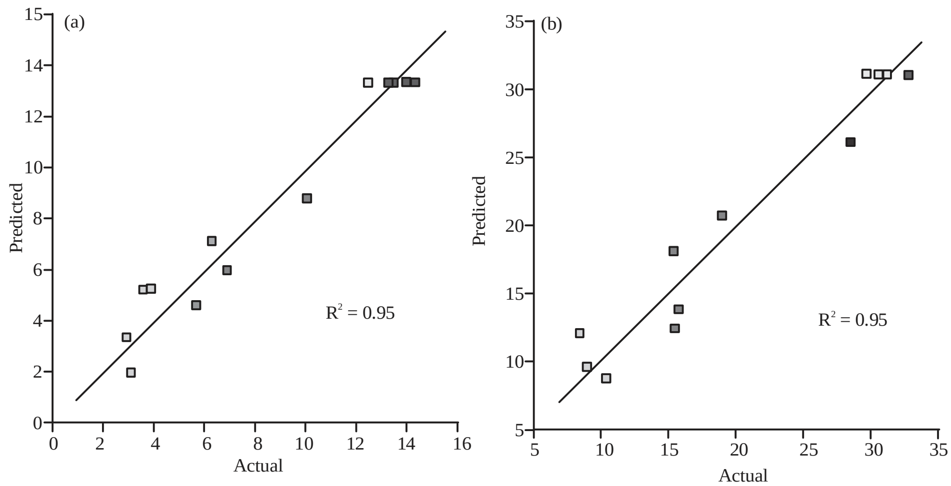

Fig. 4(a-b): Comparison of the actual values and the predicted values; a) stem samples and b) leaves samples

Table 3: The ANOVA results for the models coefficients

	Stem			Leaf	
Sources	df	Mean square	p-values	Mean square	p-values
Models	5	259.14	>0.0001**	58.36	<0.0001**
T_r	1	185.34	0.0014**	8.51	0.0058**
T_c	1	16.4	0. 194**	9.02	0.056**
$T_r \times T_c$	1	5.66	0.4429^{ns}	0.96	0.5045^{ns}
$T_r \times T_r$	1	274.53	0.0004**	78.83	0.0002**
$T_c \times T_c$	1	908.35	< 0.0001**	219.24	< 0.0001**

**Significant; ns: not significant

Table 4: The optimum operating temperatures for reactor and condenser for maximizing pyrolysis oil yield

			Bio-oil yield	
Materials	T_r (°C)	T_c (°C)	Predicted (%)	Actual (%)
Stem	523	-12	33	33.02
Leaf	494	-12	14	13.40

express the yield of stem and the yield of leaves as functions of reactor Temperature (T_r) and condenser surrounding Temperature (T_c):

$$Y_s = -106.75387+0.419855T_r-4.9829 T_c-0.000401T_r^2-0.206982T_c^2 \quad R^2 = 0.95 \tag{6}$$

$$Y_l = -52.7615+0.21255T_r-2.39996T_c-0.00021491T_r^2-0.10162T_c^2 \quad R^2 = 0.95 \tag{7}$$

The high values for coefficient of determination for both samples indicates the proximity of the experimental data and the values predicted by the model.

Figure 4 a and b show the experimental value graph versus the values predicted by Eq. 6 and 7 for the response.The high matching of the responses obtained in tests performed with their regression line indicates that the data obtained is close to the predicted data. These results indicate the suitability of fitted quadratic equations.

Figure 5a and b show the graphical representation of changes in pyrolysis oil yield (vertical axis) versus temperature change of reactor and condenser. The graphs indicate that in both samples with increasing reactor temperature, the pyrolysis oil yield is gradually increased, reaching its maximum and then gradually decreasing, indicating second-degree polynomial relationships. Since, this trend is almost uniform at all points related to the condenser temperature, indicating that there is no interaction effect ($T_r \times T_c$) between the independent variables.

Optimization of factors: The results of optimization of the two (Eq. 6 and 7 using (Eq. 5) are given in Table 4. The table indicates that the optimum conditions for producing pyrolysis oil from stem were 523°C for the reactor and -12°C for the condenser surrounding. For leaf samples, the optimum conditions were 494°C the temperature for the reactor and -12°C for the condenser surrounding. At the optimal points, the yield for stem pyrolysis oil production was 33% and for leaf was 14%

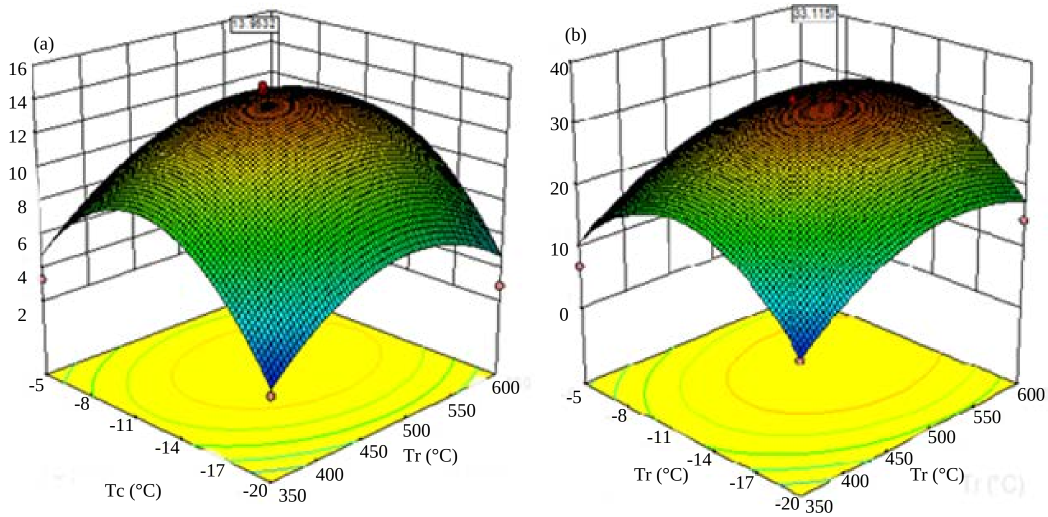

Fig. 5(a-b): The response surface for pyrolysis oil yield; a) stem samples and b) leaves samples.

(w/w). The experiments performed at the optimum conditions indicated that the yield of pyrolysis oil for stem was 33.02% and for leaf was13.4%which are very close to the theoretical values.

CONCLUSION

In this research, the effect of reactor temperature and condenser temperature on pyrolysis oil yield obtained from stem and leaf of cypress trees were studied. The HHV and LHV for stem samples was 17.08 and 16.01 MJ kg^{-1}, respectively and for leaf samples were 18.87 and 17.16 MJ kg^{-1}, respectively. The quadratic models obtained from stem and leaf samples for estimating the yields pyrolysis oils were highly fitted to the experimental data ($R^2 \geq 0.95$).The analysis of the thermal decomposition process showed that with increasing temperature, the thermal decomposition rate increased and the char level decreased and conversely, the amount of exhaust gases increased. At the optimal conditions (525°C for the reactor and -12°C for the condenser), the maximum pyrolysis oil equal to (33% w/w) was obtained for stem sample. The optimal conditions for leaves samples were 494°C for the reactor and -12°C for the condenser. At these conditions, the pyrolysis oil yield was (14% w/w).

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REFERENCES

01. Yorgun, S. and D. Yildiz, 2015. Slow pyrolysis of paulownia wood: Effects of pyrolysis parameters on product yields and bio-oil characterization. J. Anal. Applied Pyrolysis, 114: 68-78.
02. Alonso, D.M., J.Q. Bond and J.A. Dumesic, 2010. Catalytic conversion of biomass to biofuels. Green Chem., 12: 1493-1513.
03. Park, J., Y. Lee, C. Ryu and Y.K. Park, 2014. Slow pyrolysis of rice straw: Analysis of products properties, carbon and energy yields. Bioresour. Technol., 155: 63-70.
04. Luz, F.C., S. Cordiner, A. Manni, V. Mulone and V. Rocco, 2018. Biomass fast pyrolysis in screw reactors: Prediction of spent coffee grounds bio-oil production through a monodimensional model. Energy Conver. Manage., 168: 98-106.
05. Pattiya, A. and S. Suttibak, 2012. Production of bio-oil via fast pyrolysis of agricultural residues from cassava plantations in a fluidised-bed reactor with a hot vapour filtration unit. J. Anal. Applied Pyrolysis, 95: 227-235.
06. Aysu, T. and M.M. Kucuk, 2013. Biomass pyrolysis in a fixed-bed reactor: Effects of pyrolysis parameters on product yields and characterization of products. Energy, 64: 1002-1025.
07. Hmid, A., D. Mondelli, S. Fiore, F.P. Fanizzi, Z. Al Chami and S. Dumontet, 2014. Production and characterization of biochar from three-phase olive mill waste through slow pyrolysis. Biomass Bioenergy, 71: 330-339.

08. Acikgoz, C., O. Onay and O.M. Kockar, 2004. Fast pyrolysis of linseed: Product yields and compositions. J. Anal. Applied Pyrol., 71: 417-429.
09. Sensoz, S., D. Angin and S. Yorgun, 2002. Influence of particle size on the pyrolysis of rapeseed (Brassica napus L.): Fuel properties of bio-oil. Biomass Bioenergy, 19: 271-279.
10. Yu, S., J. Park, M. Kim, C. Ryu and J. Park, 2019. Characterization of biochar and byproducts from slow pyrolysis of hinoki cypress. Bioresour. Technol. Reports, 6: 217-222.
11. Selim, S.A., M.E. Adam, S.M. Hassan and A.R. Albalawi, 2014. Chemical composition, antimicrobial and antibiofilm activity of the essential oil and methanol extract of the Mediterranean cypress (Cupressus sempervirens L.). BMC Complementary Altern. Med., 14, No. 1. 10.1186/1472-6882-14-179.
12. Boukhris, M., G. Regane, T. Yangui, S. Sayadi and M. Bouaziz, 2012. Chemical composition and biological potential of essential oil from Tunisian Cupressus sempervirens L. J. Arid Land Stud., 22: 329-332.
13. Amini-Niaki, S.R. and A. Ghazanfari, 2012. Comparison of fuel and emission properties of petro diesel and sunflower biodiesel prepared by optimized production variables. Fuel, 109: 384-388.
14. Channiwala, S.A. and P.P. Parikh, 2002. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel, 81: 1051-1063.
15. Wongsiriamnuay, T. and N. Tippayawong, 2010. Thermogravimetric analysis of giant sensitive plants under air atmosphere. Bioresour. Technol., 101: 9314-9320.