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Research Article

Production of Pyrolysis Liquid from Pine Bark with Improved PID System and Analysis of Its Components by GC-MS

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Abstract **–** In this research, the bark of pine trees is procured, dried, and ground in the province of Elazığ (Türkiye). In an inert environment, the liquid of the pyrolysis vapor is condensed using a double condenser system in the improved PID-controlled pyrolysis reactor. In experimental studies, using response surface methodology (RSM) in the pyrolysis process, temperature, time, and amount of mass are optimized. Two phases are formed in the obtained pyrolysis liquid and these phases are separated with the help of a separating funnel. Low-density compounds are in the upper phase, and high-density liquid is in the lower phase. According to the results, maximum efficiency is obtained at 376 °C, 185 minutes, and 519 grams of pine bark powder. The efficiency of wood vinegar is found by the ratio of the amount of acetic acid to components other than water. The efficiency is calculated by gas chromatography-mass spectrometry (GC-MS) values. Experimental data and RSM model results have been evaluated by statistical analysis. Considering the amount, color, and components of the pyrolysis liquid, an evaluation can be made about the quality of this liquid. Also, as the particle size of the pine bark decreases, the surface area increases, so the pyrolysis time reduces.

Keywords – Pine Bark, Wood Vinegar, Pyrolysis, RSM Optimization, Efficiency

I. INTRODUCTION

Wood vinegar is obtained by resting the liquid formed by the distillation of steam, gas, and smoke released during the pyrolysis process of biomass. Wood vinegar contains a very high amount of water and consists of acetic acid. Other acids, alcohols, phenols, esters, carbonyl, furans, and other organic compounds are found in wood vinegar [1].

Wood vinegar improves the quality of the soil, provides a plant growth regulator, protection against plant pests and diseases. It is preferred in agricultural activities due to the high amount of nitrogen, phosphorus, and potassium it contains. Wood vinegar increases the functionality of the soil and enables the soil to benefit from the compounds (elements) easily. The density of wood vinegar is 1005-1016 kg/m^3, its pH is 2-4, and the dissolved tar content is between 0.2-0.9 wt%. Wood vinegar provides the organic matter balance of the soil and increases the quality of the soil. It is effective in the germination of seeds, the growth of the plant, the yield of the crop, and the fight against diseases and pests. Besides, it helps to decrease pH in the soil, balance the organic components, and the functionality of microorganisms. Wood vinegar ensures both the recovery of biomass waste and its transformation into an environmentally friendly product. If the biomass is heated in an inert environment, it turns into biochar with the effect of temperature, and when the steam/gas released during this process is cooled, wood vinegar is obtained. An oily liquid with different densities is observed in the upper phase, a dense tar in the lower phase, and raw wood vinegar in the middle phase. Wood vinegar consists of a yellowish-brown liquid and constitutes approximately 7 % of the total biomass [2].

Vinegar from trees such as oak, bamboo, coconut, and apple can be produced in the research in the literature. Different tree species are used as a source of wood vinegar and naturally regulate the bioactivity of the soil. It also shows antioxidant and antimicrobial activity in protecting plants against various pests [3].

Recently, the widespread use of wood vinegar in the agricultural sector has increased its production and consumption. It is necessary to know the properties of wood vinegar, which is also used outside of agricultural use. Detailed studies on the physical and chemical structure of wood vinegar are still ongoing. For example, wood vinegar is naturally used as an insect repellent and preservative [4].

Pyrolysis is a method generally used to obtain wood vinegar by thermal decomposition of organic materials. With the pyrolysis system, biomass wastes undergo thermal decomposition in high temperature and airless conditions. In this system, fast and slow pyrolysis processes can be performed according to the heating rate. Fast pyrolysis is an advanced process where the biomass is heated to a temperature of about 500 °C for less than 2 seconds. The hemicellulose in the biomass decomposes rapidly in the temperature range of about 200 to 300 °C. Cellulose decomposes in the temperature range of about 300 to 400 °C and lignin exhibits thermal degradation behavior in the range of 250 to 500 °C. There are many physical and chemical differences between the initial structure of biomass and its final state [5].

The originality of this study is to obtain high-efficiency pyrolysis liquid from biomass waste with the newly improved PID-controlled reactor. Product quality is increased by optimizing both experimental working conditions and waste biomass amounts by RSM [6].

II. MATERIAL AND METHOD

The pine shells supplied in Elazığ (Türkiye) are ground and prepared for the pyrolysis process. With the newly developed PID-controlled reactor system, optimum conditions are provided and pyrolysis liquid is produced (Figure 1).

GC-MS analysis of the pyrolysis liquid obtained in the experimental studies has been analyzed by Shimadzu brand QP 2010 Ultra model device. Pine bark amount, pyrolysis time, and pyrolysis temperature are modeled according to RSM. Obtained results have been evaluated by statistical analysis.

Figure 1. PID-controlled pyrolysis reactor system

Figure 2. Pine bark and its powder prepared for pyrolysis

III. RESULTS AND DISCUSSION

It is understood from the statistical analyses that the experimental data give results compatible with RSM [7]. It is seen that the values of R^2 (0.9727), adjusted R^2 (0.9481), predicted R^2 (0.9185), and standard deviation (2.91) are compatible. The variation of the effective parameters according to RSM results in the experiments performed in the pyrolysis reactor is shown in Figure 3 and Figure 4. Besides, the effect of biomass amount and temperature on pyrolysis efficiency has been evaluated in Figure 5 and Figure 6.

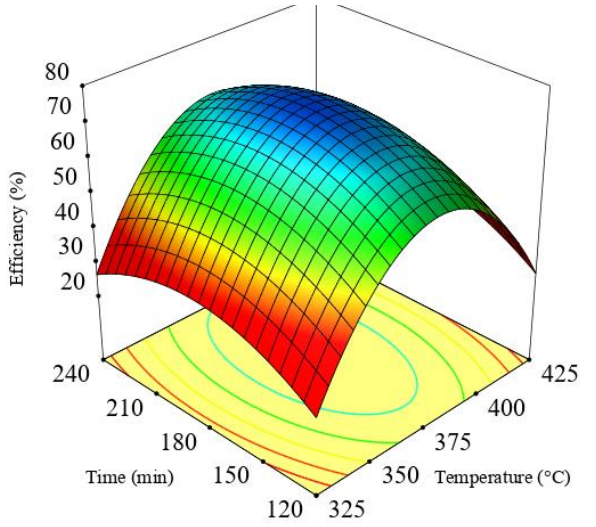

Figure 3. Effect of time and temperature on pyrolysis efficiency (3D)

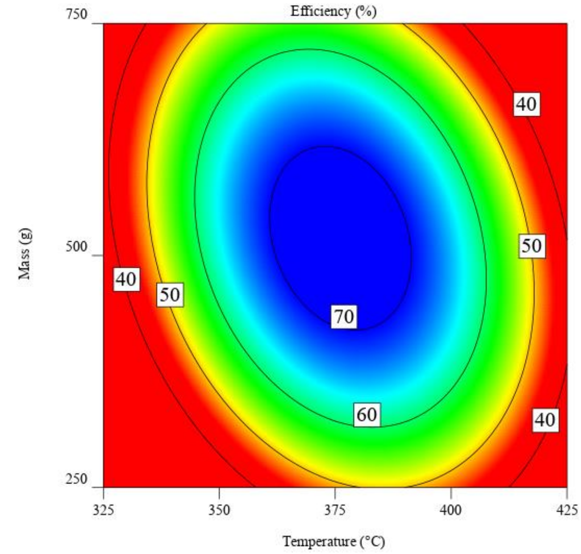

Figure 6. The effect of the amount of biomass used in the system and the temperature on the efficiency (2D)

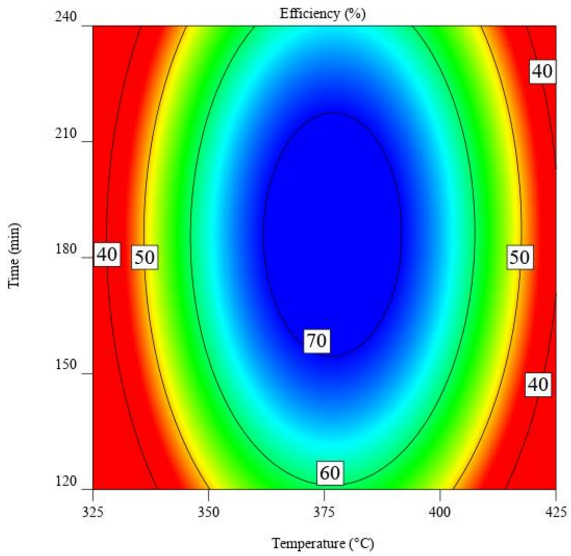

Figure 4. Effect of time and temperature on pyrolysis efficiency (2D)

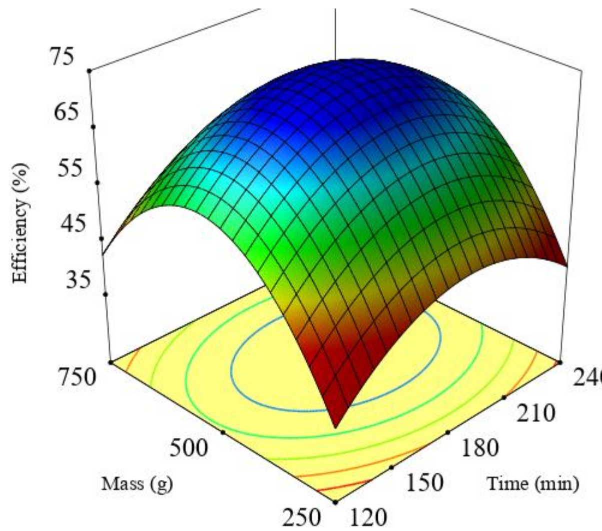

Figure 7. The effect of the amount of biomass used and the pyrolysis time on the efficiency (3D)

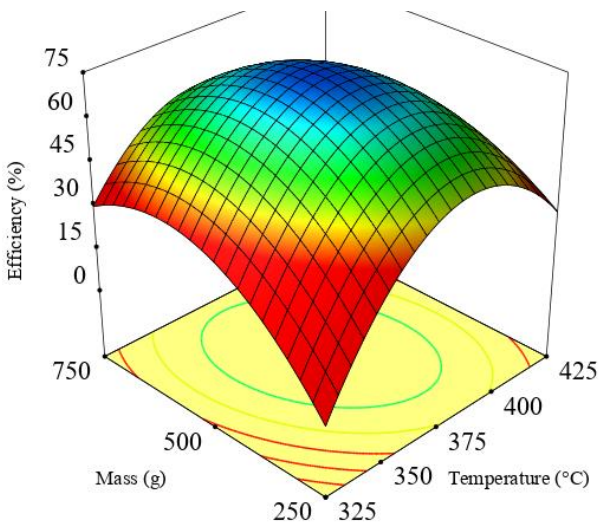

Figure 5. The effect of the amount of biomass used in the system and the temperature on the efficiency (3D)

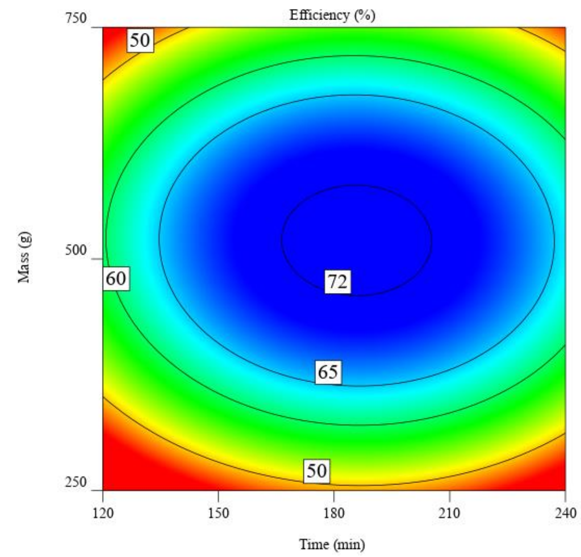

Figure 8. The effect of the amount of biomass used and the pyrolysis time on the efficiency (2D)

In the equation below, the percent efficiency (E) is given as a polynomial function of temperature (T), time (t), and mass (M). The relationship between experimental data and RSM is expressed in this model equation.

$$E (\%) = -2263.88085 + 10.90659 \cdot T + 1.12547 \cdot t + 0.698985 \cdot M$$
$$+0.000118 \cdot T \cdot t - 0.000933 \cdot T \cdot M - 0.000024 \cdot t \cdot M$$
$$-0.013883 \cdot T^2 - 0.003113 \cdot t^2 - 0.000331 \cdot M^2$$

Table 1 shows the components of the pyrolysis liquid obtained from pine bark according to GC-MS analysis results. As seen in the table, there are many important compounds in the composition of wood vinegar obtained from the pyrolysis of pine bark. The amount of water (H_2O) in the composition of wood vinegar given in Table 1 is determined as 76.78 wt.%. The sum of the amount of water and the components given in Table 1 represents wood vinegar (100 wt.%).

Table 1. GC-MS analysis results of wood vinegar

Components	**%**
Acetic acid, methyl ester (CAS) Methyl acetate	0.91
Acetic acid (CAS) Ethylic acid	6.04
2-Propanone, 1-hydroxy- (CAS) Acetol	1.5
Furan, Tetrahydro-2-Methoxy-	0.33
2-Butanone, 3-hydroxy- (CAS) Acetoin	0.42
Captafol	0.02
Propanoic acid (CAS) Propionic acid	1.75
1,2-Ethanediol (CAS) Ethylene glycol	0.45
Aldicarb	0.06
1-Hydroxy-2-butanone	0.3
Propylene Glycol	0.07
Pyridine, 2-methyl- (CAS) 2-Methylpyridine	0.14
Methyl Thioasetohydroxamate	0.57
Furancabonsaeurechlorid, Tetrahydro-	0.62
Aldicarb	0.13
Acephate	0.09
2-Cyclopenten-1-one (CAS) Cyclopentenone	0.13
2-Butenoic acid (CAS) Crotonic acid	0.09
2,5-Dimethoxytetrahydrofuran	0.11
1,2-Ethanediol, monoacetate (CAS) 2-Hydroxyethyl acetate	0.63
1,2-Ethanediol, diacetate (CAS) Ethylene diacetate	0.14
Tolylfluanid metabolite	0.03
5,9-Dodecadien-2-one, 6,10-dimethyl-, (E, E))-	0.48
Spirodiclofen	0.06
Dazomet	0.06
2,5-Hexanedione (CAS) Diacetonyl	0.29
Tebuthiuron	0.52
Butanoic acid, 4-chloro-	1.07
2(5H)-Furanone	0.63
Hymexazol	0.05
2-Cyclopenten-1-one, 3-methyl-	0.42
Aldicarb deg.	0.3
2-(1-Naphthyl)acetamide	0.43
Phosphonic acid, (p-hydroxyphenyl)-	0.8
Oxamyl	0.5
Hymexazol	0.05
2-Cyclopenten-1-one, 2-hydroxy-3-methyl- (CAS) Corylon	2.45
Esprocarb	0.11
Molinate	0.47

IV. CONCLUSIONS

In this study, experimental studies have been carried out by optimizing the amount of biomass, pyrolysis temperature, and time by RSM. RSM results have been determined by statistical analysis and their compatibility with the experimental data is compared. According to the results, 519 grams of pine bark gives the highest yield at 376 °C and 185 minutes. Obtaining wood vinegar at high temperatures both leads to carbonization and increases the formation of tar. Considering the working conditions of PID controlled system, both the use of a high amount of biomass and the long pyrolysis time reduce the energy efficiency [8]. According to GC-MS results, the acetic acid ratio in wood vinegar is taken as the effective parameter in the pyrolysis efficiency. Also, the results have been evaluated by taking into account the color of wood vinegar, the tar precipitated in the lower phase, and the richness of the components.

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