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Catalytic Pyrolysis of Plum Seed

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Abstract

In this study, pyrolysis and catalytic pyrolysis of the plum seed was investigated. For this purpose, the characteristics of the raw materials were determined by proximate analysis (moisture, ash, volatile matter, fixed carbon), structural analysis (holocellulose, hemicellulose, hemicellulose, lignin, oil, protein and extractive material) and ultimate analysis .The pyrolytic behavior of the feedstocks was studied by thermogravimetric analysis. Then pyrolysis temperature, which is a significant pyrolysis parameter, investigated the effect of heating rate on pyrolysis product yields. When the pyrolysis temperature is 550°C, the nitrogen flow rate is 100 cm^3/min and the heating rate is 100°C/min, the highest liquid product yield is achieved. In order to improve the quality of the liquid product obtained as the next process, catalytic pyrolysis of the raw material in optimum conditions is carried out. Catalytic pyrolysis experiments were carried out by adding 10% of Purmol CTX-1 catalyst to the raw material. Liquid products are characterized with spectroscopic and chromatographic methods such as GC-MS, FT-IR, ^{1}H-NMR**Keywords:** Catalytic pyrolysis, plum seed,bio-fuel

1. Introduction

Biomass catalytic pyrolysis has some advantages like promoting the yield of energy and getting directional chemical products. Catalytic pyrolysis consists of two stages; firstly pyrolysis of biomass takes places and catalytic transformation of pyrolysis vapors occurs. In the first step, biomass is converted into pyrolysis vapors, non-condensable gases and bio-char when it is heated. Then, the vapors are met with the catalyst surface. In this surface, the oxygenated compounds can be turned into aromatics and aliphatics via deoxygenation (Aysu, 2015). Catalysts take a role not only making easier the cracking of carbon-carbon bonds and de-oxygenation reaction but also producing bio-oil that is lower in oxygenates, has a higher calorific value and better hydrocarbon distribution. Thus, the quality and stability of bio-oil are enhanced, making the handling; upgrading and transporting of bio-oils are easier as well as reduction of processes costs (Thangalazhy-Gopakumar et al., 2011).

In the present work, laboratory scale results were evaluated on thermal and catalytic pyrolysis of plum seed peel. In the thermal pyrolysis experiments, plum seed peel pyrolysis was performed to investigate the effect of temperature, heating rate on product distributions. In the catalytic part, the effect of purmol-CTX-1commercial catalyst on product yields and bio-oil compositions were studied and compared with thermal pyrolysis.

2. Material and Methods

2.1 Characterization of Sample

Plum seed was provided by a juice factory in /Turkey. The seed samples were dried naturally in open air in the dark room up to two months, ground, milled and sieved. An average particle size was calculated as 1.22 mm. Proximate analysis was applied in order to detect the volatile matter, ash, moisture and fixed carbon. Leco CNH628 S628 elemental analyzer was used to detect carbon, hydrogen, nitrogen and oxygen contents by using helium, dry air and oxygen gases. The proximate, ultimate and structural analysis of the plum seed was carried out and results were presented in Table 1.

2.2 Pyrolysis Experiment

The pyrolysis experiments were carried out under nitrogen atmospheres using laboratory scale reactor described elsewhere (Pehlivan, 2017). The experiments were performed in order to determine the catalyst effect on the pyrolysis yields. The experiments were implemented in catalyst/biomass ratio of 10% at the optimum conditions for all these experiments.

2.3 Product analysis

The obtained bio-oils were characterized using several chromatographic and spectroscopic techniques including elemental analysis, FT-IR,^{1}H-NMR analysis, GC-MS and column chromatography.

Table 1. Properties of pulm seed

	wt. %		wt. %
Moisture[c]	8.87	C[a]	43.50
Ash[b]	0.91	H[a]	5.24
Volatile	83.84	N[a]	0.73
Fixed	6.38	O[a]	50.53
Cellulose[c]	44.58	H/C	1.45
Lignin[b]	31.97	O/C	0.87
Oil[c]	7.17		
	18.30	HHV(MJ/kg)	13.16

[a] Dry-ash-free basis. [b] Dry basis[c] As received. HHV:Higher Heating Value

3. Results and Discussion

3.1 Yields of pyrolysis products

Catalytic pyrolysis findings are compared with the results of without catalysist pyrolysis.. As seen from Fig. 1, the use of catalyst caused a reduction in the amount of solid and gas product yield. Maximum oil yield was achieved with purmol CTX-1 as 31.02%.

3.2 Characterization of bio-oils

In Fig 3, GC-MS chromatogram of catalytic pyrolysis bio-oil were shown. The compounds identified in the bio-oils have been classified as follows: Straight chain alkanes and alkenes ranging between C_{13}–C_{30}, monoaromatic compounds, PAHs, phenols, ketones, carboxylic acids, aldehydes, triterpenoid compounds, and nitrogenated compounds. Phenolic compounds are also main products obtained by pyrolysis. Because of being industrially important, phenolic compounds could be utilised to produce solvents or phenolic-based adhesiveslike novolac and resole resins (Saraçoğlu et al., 2017). Results of ^{1}H-NMR for the bio-oil is given in Table 2. The ^{1}H NMR spectra were divided into three regions of interest based upon the chemical shifts of specific proton types. Aliphatic resonances occur in the chemical shift region 0.5-3.0 ppm, olefinics resonances occur between 4.5and 6.3 ppm region and aromatic resonances occur in the 6.0-9.0 ppm region.

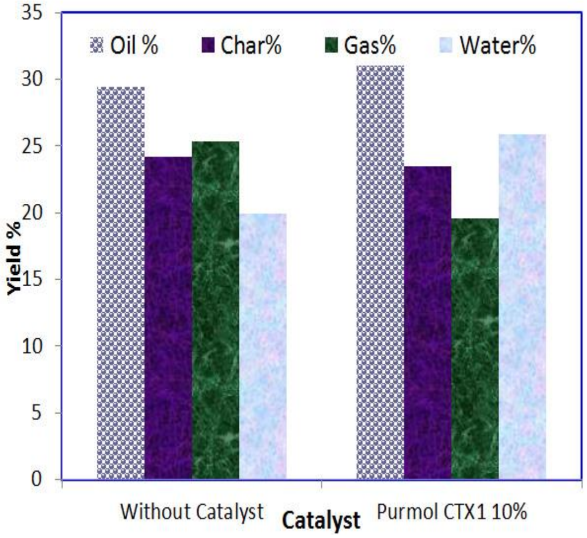

Figure 1. Products yield distributions of thermal and catalytic experiments.

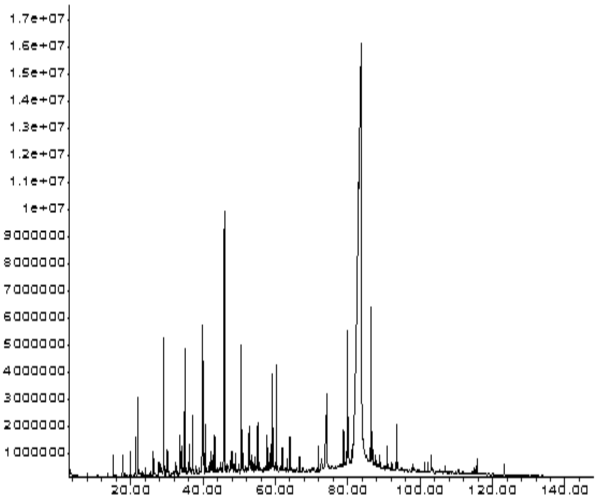

Figure 2. GC-MS chromatogram of catalytic pyrolysis bio-oil

Table 2 Results of ^{1}H-NMR for the bio-oil

Hydrogen type	Chemical shift (ppm)	Biooil (%)^a
CH_3 γ or further from an aromatic ring	1.0-0.5	4.09
CH_3; CH_2 and CH γ or further from an aromatic ring	1.6-1.0	16.47
CH_2 and CH β an aromatic ring (naphthenic)	2.0-1.6	6.62
CH_3; CH_2 and CH α to araomatic ring	3.3-2.0	27.04
ring-joining methylene (Ar-CH_2-Ar)	4.5-3.3	19.30
phenolic (OH)olefinic proton	6.5-5.0	8.77
aromatic	9.0-6.5	17.69

Catalyst choice and evaluation for higher product selectivity were essential in industrial applications. The study of catalyst for the pyrolysis of oil is very important for the future of biorefinery.

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