

Effects of Catalyst on Pyrolysis of Laurel (*Laurus Nobilis L.*) Seed in a Fixed Bed Tubular Reactor

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In this study, the daphne seed (*Laurus nobilis L.*) was used as biomass sample for catalytic pyrolysis using (Ni/Al₂O₃) commercial catalyst (Criterion-454) in the nitrogen atmosphere. Experimental studies were conducted in a fixed bed tubular reactor with a heating rate of 300 °C·min⁻¹, a final pyrolysis temperature of 600 °C and particle size of 0.6-0.85 mm. In order to establish the effect of catalyst ratio on the pyrolysis yields, experiments were conducted at a range of catalyst ratios between 0, 1, 5, 10, 20 % (w/w). The non-catalytic and catalytic pyrolysis oils were characterized by elemental analysis and some spectroscopic and chromatographic techniques. Catalytic pyrolysis enhanced the yield and physical properties of the pyrolysis oils and confirmed that lower feed to catalyst ratio increased the pyrolysis oil yield. The oil was rich in hydrocarbon and thus termed as catalytic pyrolysis oils which can be used as fuel.

1. Introduction

The diminishing reserves and apparent negative effects such as greenhouse gases and acid rain of fossil fuel have led the world community to recognize the importance of renewable and cleaner energy in recent years. The recovery of energy from a renewable source like biomass involves chemical, biochemical and thermo chemical processes, depending on the nature of the source. The main advantages of using biomass are its negligible sulphur, nitrogen and metal content. The utilization of biomass for energy generation has led to reduced carbon dioxide, sulphur dioxide emissions and importantly prevents the greenhouse effect and acid rain. The net flow of carbon dioxide to the atmosphere, and thereby the global potential, is reduced when fossil fuels are replaced with sustainable produced biomass. Consumption of agricultural residues for energy production would also reduce the environmental damage.

Among the thermo chemical processes, pyrolysis has become an attractive alternative because of the ease of operation. Its suitability to produce fuel for energy production and as feed stock for chemical industries, relatively few polluting emissions, carbon dioxide neutral cycle and ease of reproduction makes pyrolysis oil a favourable option. The proportion of gas, liquid and solid products depend very much on the pyrolysis technique used and on the reaction parameters. Depending on the operating conditions, the pyrolysis process can be divided into three sub classes: conventional pyrolysis (carbonization), fast pyrolysis and flash pyrolysis. Slow pyrolysis processes are performed at a low-heating rate and a long residence time. The longer residence times can cause secondary cracking of the primary products reducing yield and adversely affecting oil properties. In additions, a low heating rate and long residence time may increase energy input. All of these are not attractive for commercial application of liquid fuel production. At present, the preferred technology for production of oily products is fast or flash pyrolysis at high temperatures with very short residence times (Demirbaş, 2004). The pyrolysis oil from biomass waste was found to be highly oxygenated and complex, and chemically unstable. Thus, the liquid products still need to be upgraded by lowering the oxygen content and removing residues (Tsai et al., 2007).

Catalytic pyrolysis is one which can increase the yield of liquid as well as the quality of pyrolytic oil. It was reported that pyrolytic oil having higher oxygen content reduces the storage stability (Dumesic, 2005). To improve the quality of crude oil for biofuel applications and to reduce the upgrading costs, biomass pyrolysis can be carried out in the presence of suitable catalysts (Park et al., 2010). Complete deoxygenating of oil can meet the fuel properties of transportation fuel such as diesel and petrol.

Literatures disclosed that catalyst with silica and alumina composition and oxides of metal increased the yield and fuel properties by decreasing oxygen content of the pyrolytic oil (Mante and Agblover, 2011). Fast pyrolysis oil upgraded by hydro deoxygenation can be produced at a very competitive price compared to other biomass conversion technologies. The catalytic treatment can either be in situ, i.e. adding catalyst particles to the reactor, or ex situ, i.e. secondary conversion of the produced pyrolysis vapour fraction. The desired function of the catalyst is in both cases the removal of oxygen containing compounds and the catalytic cracking of high molecular weight compounds.

The main chemical reactions are hydrocracking, decarbonylation, decarboxylation, hydrodeoxygenation, cracking, and hydrogenation. However, the catalytic hydrotreatment of pyrolysis oils is far from the commercial scale in contrast to the conventional refining, and intensive research is required (Liu, 2014). The catalytic systems used in hydrodeoxygenation of bio-oil and its model compounds were conventional sulfided NiMo and CoMo alumina-supported desulfurization catalysts and noble metal based catalysts (Pt, Pd, Rh, Ru) (Garcia et al., 2002). These catalytic systems possessed high activity in target hydrodeoxygenation process, but some of their disadvantages were also revealed (Tomishige et al., 2007). The main disadvantage of using noble metal based catalysts is high cost that makes their use in hydroprocessing of bio-oils economically unprofitable. As an alternative for the sulfided catalysts and noble metal based catalysts mentioned above, non-sulfided systems based on transition metals (Ni, Fe, Co, Mo, etc.) were considered: systems with the metallic state of the active component transition metal oxides, transition metal phosphides and amorphous boron-containing catalysts. They catalyse hydrogenation and hydrodeoxygenation reactions and are cheaper than noble metal based ones (Wang et al., 2011). Ni-based catalysts possess high activity and improved stability in hydrodeoxygenation of oxy-organic compounds including bio-oil (Liu, 2012).

Turkey has considerable sources of renewable, and among these energy sources, biomass will become precious sources of energy in the future since Turkey is an agricultural country and has abundant biomass sources. Sunflower, cotton, rape, safflower and euphorbia species are among the most promising renewable sources that have already been studied from the pyrolysis parameters and fuel properties. As an addition to biomass diversity of Turkey a wild growing evergreen tree Laurel is focused for possible use as a renewable fuel source. Laurel (*Laurus nobilis* L.) is a plant native to the southern Mediterranean region and is widely cultivated mainly in Europe and the USA as an ornamental plant. It is grown commercially for its aromatic leaves in Turkey, Algeria, Morocco, Portugal, Spain, Italy, France and Mexico. In Turkey, the essential oil of *L. nobilis* is produced from leaves, and for its wood, which is very suitable for fence posts or supporters of wine plants. On the other hand Laurel berry contains, substantial amounts of fixed oil consisting mainly of odorless lauric acid, myristic acid and related compounds. From this point of view, laurel seed is of importance as a very important candidate of potential source of renewable fuels and chemical feedstock in Turkey.

In this study, daphne seed (*Laurus nobilis* L.) was chosen as the renewable energy source and in situ catalytic pyrolysis of sample conducted in a fixed bed tubular reactor. The effects of catalyst Criterion 424 (Ni/Al₂O₃), widely used in the petrochemical industry ratio, on the product yields was investigated with the aim to identify optimum process conditions for maximizing the pyrolysis oil yield. Catalytic pyrolysis oils were characterized by using some spectroscopic techniques such as FTIR, ¹H NMR and elemental analysis and obtained results compared with non-catalytic pyrolysis oil.

2. Materials and methods

2.1 Materials

The samples of daphne seed (*Laurus nobilis* L.) were obtained from the town of Silifke, located in the Mediterranean region of Turkey and selected as reference biomass feedstock, particle size was between 0.6-0.85 mm. The commercially available Ni-Mo/γ-alumina catalyst, Criterion 424, its oxide composition being MoO₃ (19.5% w/w), NiO (4% w/w), and P₂O₅ (8% w/w) were selected for the catalytic pyrolysis of sample. To minimize the water accumulation in the final liquid product, this catalyst was calcined in air at 400°C for 2 h to decrease the catalyst bound/absorbed moisture content to below 1 wt.%

2.2 Characterization of raw materials

The samples of daphne seed were characterized according to their proximate and ultimate analysis (ASTM E870-82). Proximate analysis gives the idea about the % of moisture, volatile, ash and fixed carbon content in the respective samples. The ultimate analysis was carried out in CHNSO elemental analyser (A CHNS-O Fisions, EA 1108) to know the elemental composition.

Table 1. Proximate and ultimate analysis of daphne seed

Char Characteristics	Daphne seed
<i>Proximate analysis(wt.%, as received)</i>	
Moisture	6.8
Volatile	85.6
Fixed C	5.8
Ash	1.8
<i>Ultimate analysis(wt%, daf.basis)</i>	
Carbon	54.2
Hydrogen	7.6
Nitrogen	2.7
Oxygen (<i>by difference</i>)	35.5
Calorific value (MJkg ⁻¹)	22.9

2.3 Experimental set up and procedure

Fast pyrolysis experiments were carried out under nitrogen atmosphere in a fixed bed tubular reactor with a length of 90 cm and an inner diameter of 8 mm, made of 310 stainless steel. Five g of biomass sample was mixed with catalyst at different feed to catalyst percentages either 1 %, 5 %, 10 %, or 20 % by weight and then placed in the reactor. The sweep gas velocity of 100cm³min⁻¹ was controlled and measured by a rotameter. The sample was heated at a heating rate of 350 °C·min⁻¹ to the final temperature of 600 °C and held at that temperature for 30 min or until no release gas observed. Heating rate and pyrolysis temperature were controlled by a proportional-integral-derivative (PID) controller. After pyrolysis, char yield was determined from the overall weight losses of the reactor tube. The liquid phase was collected in a glass liner located in a cold trap maintained at about 0 °C. At the end of the experiments, the bio-oil fraction was separated from the water by use of dichloromethane and weighed. The weight gains for the liquids trap were corrected for the amounts of water present to give the actual oil yields. As for gas and water yield was determined by overall material balance (Onay 2007).

2.4 Characterization of catalytic pyrolysis oil

The non-catalytic and catalytic pyrolysis oils analysed in this study have been obtained in the experimental condition that has given maximum oil yield. A CHNS-O Fisons, EA 1108 instrument was used to determine the elemental composition of the samples. The calorific value of the samples was determined (ASTM 3286). The values reported are the gross heat of combustion at constant volume.

The IR spectrums of the pyrolysis oils were made using a Perkin Elmer FT-IR Spectrometer Spectrum 2000. The ¹H NMR of the oils was obtained at an H frequency of 500 MHz using Bruker BioSpin GmbH instrument. The samples were dissolved in chloroform-d.

3. Result and discussion

3.1 Characterization of raw material

The proximate and ultimate analysis of the daphne seed was carried out and presented in Table 1. The result confirmed that daphne seed restrained maximum volatile matters (85.6 %) with lower of moisture (6.8%) and ash (1.8%) contents. Higher moisture of biomass has a more tendency to decompose resulting in energy loss during storage. More volatile matter produces more liquid and gaseous fuel during pyrolysis. The raw material contains higher percentage of volatile matter and less fixed carbon, makes them more useful for pyrolysis and gasification than solid fuel.

3.2 Influence of catalyst on product yields

Catalytic pyrolysis of daphne seed was carried out at four different feed to catalyst ratio 1 %, 5 %, 10 %, or 20 % by weight at pyrolysis temperature of 600 °C and a heating rate of 350 °C·min⁻¹. The pyrolysis oil, char and water+gas yields (wt.% based on biomass feed) obtained by the in situ catalytic upgrading of biomass pyrolysis products are visualized in Figure 1. These values are compared to the yields obtained for the non-catalytic experiment. The char product yield was reduced slightly when compared to the non-catalyst experiments with catalyst also. It can be seen from Figure 1 that, there is no significant change in the char yields with different catalyst ratios. This indicates that catalyst ratio has no significant effect on pyrolysis conversion. Thermal cracking initially breaks relatively weak aliphatic bonds and it helps to release the tar. In the catalyst pores, formed rather reactive free radicals showed a trend to provide

products in favor of liquid product yield. The pyrolysis oil yield increase with use of catalyst. It was established that the yield of pyrolysis oil yield rises only slightly in conjunction with increasing catalyst ratio and reaches its maximum with catalyst ratio of 5 %. The pyrolysis oil yield, which was 35.2 % without catalyst, reached the maximum value of 38.4 % by using this commercial catalyst ratio of 5 %. As a result, pyrolysis oil yield increase about 9.1 wt.% at catalytic pyrolysis conditions. Catalytic pyrolytic oil yield was not increased much with more use of catalyst.

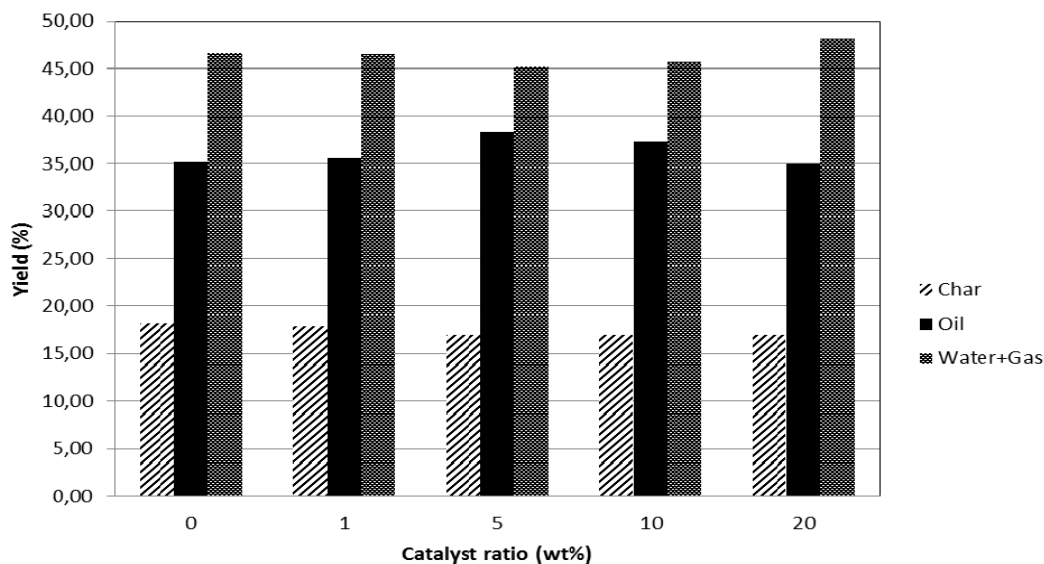


Figure 1. Yields of products in catalytic pyrolysis experiments

3.3 Influence of catalyst on pyrolytic oil

Table 2 represents the elemental composition and HHV ($\text{MJ}\cdot\text{kg}^{-1}$) of the non-catalytic and catalytic pyrolytic oil. As it can be seen in Table 1 and 2, pyrolytic oil contains less amounts of oxygen content than that of the original feedstock. The significant decrease in oxygen content of the pyrolytic oil compared to the original feedstock is important, because the high oxygen content is not attractive for the production of transport fuels. In general, oxygen content of pyrolytic oil is higher which decreases the stability as well as the calorific value. It can be seen in Table 2, the oxygen content of the oil without catalyst is 33.5 %. It fell to about 29 % with Criterion-454 under catalytic pyrolysis conditions. Clearly, the action of the catalysts in removing the oxygen from the biomass derived pyrolysis oils with the formation of CO_2 , CO and H_2O is evident from the much reduced oxygen content of the oils. The calorific value of pyrolytic oil was found to be 24.4 MJ kg^{-1} . This results in increase in calorific value of pyrolytic oil. In case of using catalyst, the oxygen content decreased about 13-16 % and calorific value of pyrolytic oil increased about 11-14 % compared with non-catalytic pyrolytic oil.

Table 2. Elemental composition and HHV of the pyrolysis oils

Experiment condition	(wt%, db)				HHV (MJkg^{-1})
	C	H	N	O ^a	
Non-catalyst	56.2	7.9	2.4	33.5	24.4
Catalyst ratio of 5%.	60.2	8.4	2.2	29.2	27.2
Catalyst ratio of 20%.	61.1	8.6	2.1	28.2	27.9

^aBy difference

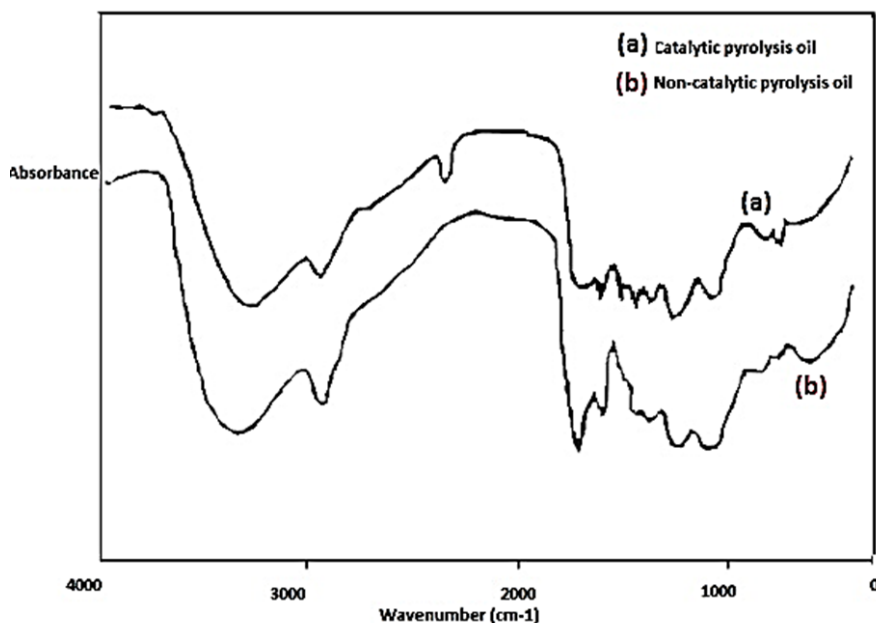


Figure 2. The IR spectrum of the pyrolysis oils

FTIR analysis provides an infrared spectrum which can be used as a fingerprint for the identification of functional groups of unknown compounds. Each and every molecule or the functional groups attached to the molecule produce characteristic and reproducible absorption in the spectrum. This information helps to indicate whether the molecule is linear or branched chained aliphatic or aromatic compound. The IR spectrum of pyrolysis oils were given in Figure 2. The catalytic pyrolysis oil with a lower oxygen content resulted in a decrease in the peak adsorption of stretching C=O ($1,750-1,650\text{ cm}^{-1}$); of stretching O-H ($3,600-3,200\text{ cm}^{-1}$) indicating the presence of phenol and alcohol; of stretching C-O ($1,300-950\text{ cm}^{-1}$); and of bending O-H. There were changes in the functional group composition of oils with and without catalyst. The peaks at $1,750$ and $1,650\text{ cm}^{-1}$ and between $3,600$ and $3,200\text{ cm}^{-1}$, are oxygenated compounds, and these peaks showed a markedly decreased with catalyst compared to the non-catalytic oil, indicating that oxygenated compounds are significantly decreased in concentration in the pyrolysis using catalyst. Several literatures have given the similar FTIR results of different pyrolytic oil (Zhou et al., 2010). The FTIR analysis of catalytic pyrolysis oil gives the strong evidence that the pyrolytic oil may be used as a fuel oil. The ^1H NMR distribution of the pyrolysis oils are given in Table 3. Results of the ^1H NMR analysis show that the pyrolysis and catalytic pyrolysis oils mainly contain aliphatic protons at carbon atoms bonded to other aliphatic carbon atoms. The amount of olefinic protons decreased with catalytic pyrolysis. On the contrary, the catalytic pyrolysis oils contained more concentration of single ring aromatic compound and aliphatic groups bonded to aromatic rings than non-catalysed pyrolysis oil.

Table 3. ^1H NMR results of the pyrolysis oils

Sample(% in weight)			
Hydrogen environment	Range (ppm)	Non -catalyst	Catalyst ratio of 5 %
Aromatic	6.3-9.3	0.82	3.34
Alkene	4.5-6.3	7.97	3.68
Aliphatic adjacent to oxygen	3.3-4.5	5.12	1.04
Aliphatic adjacent to aromatic-alkene group	1.8-3.3	10.21	17.56
Other aliphatic (bonded to aliphatic only)	0.4-1.8	75.88	74.38

4. Conclusion

The pyrolysis of daphne seed, in a fixed-bed reactor at the fast pyrolysis conditions was examined in relation to catalyst ratio on the pyrolysis product yields and their structure. The maximum oil yield of 39.5% with Criterion-454 catalyst have been achieved with to catalyst ratio of 5% at the final pyrolysis temperature of 600°C, the heating rate of 300°Cmin⁻¹, the sweep gas flow rate of 100 cm³min⁻¹ at the fast pyrolysis in situ conditions. Taking into account the pyrolysis oil yield in the catalyst ratio of 5%, it can be clearly seen that the oil yield increased about 10,9wt.% at catalytic pyrolysis conditions. In particular attention is paid to the catalyst capabilities to suppress coke and gas formation, to reduce oxygen and modify its functionalities in the oil and to increase the yield of the hydrocarbon fraction. Chemical class fraction, ¹H NMR analysis and elemental analysis of the oils showed that oxygenated species decreased with using catalyst in the experiments. Furthermore, pyrolytic oil obtained catalytic pyrolysis has less oxygenated components important for their stability, for handling and upgrading purposes. The catalytic pyrolysis oil could be used for co-feeding petroleum refinery units in the production of transportation fuels.

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