Chapter 30
Effect of Heterogeneous Catalyst on Esterification of Pyrolysis Oil

Praveen Ghodke and S. Vamsi Krishna

Abstract The bio-oil from fast pyrolysis of biomass cannot be used effectively as engine fuel because of its high corrosiveness and instability mainly due to substantial amounts of organic acids and reactive aldehydes. In this paper treatment of acids in the bio-oil was focused and esterification with different catalyst to convert the acids. Synergistic interactions among reactants and products were determined. Acid-catalyst removed water and drove the esterification reaction formation equilibria toward ester products. Effect of Amberlyst-15 on different acids present in the bio-oil was carried out and characteristics properties of bio-oil shown after treatment were improved. Catalyst characterization was carried and observed that carbon deposition on the surface of catalyst reduces the activity of the Amberlyst-15. The catalysts with high surface area, large pore size distribution, and strong acid sites may be beneficial for the esterification reaction.

Keywords Bio-oil · Esterification · Amberlyst-15 · Pyrolysis

30.1 Introduction

One of the main fields of energy consumption is the transportation sector, constituting about one fifth of the total [1]. This requirement constitutes one of the major challenges of the near future, as present fuels primarily are produced from crude oil and these reserves are depleting [2]. Substantial research is being carried out within the field of energy in order to find alternative fuels to replace fossil fuels. The optimal solution would be renewable energy resource which is sustainable and will decrease the CO_2 emission. Biomass derived fuels could be the prospective fuels of tomorrow as these can be produced within a relatively short cycle and are considered benign for the environment [3].

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Fast pyrolysis can directly produce a liquid fuel from biomass which can be readily stored or transported [4–10]. A large variety of applications for bio-oil have been proposed. Examples are the use as a fuel in boiler systems, stationary diesel engines, gas turbines and sterling engines [5, 11]. However, Bio-oil has many inferior properties, such as low heating value, high oxygen content, high water content, acidity, instability, and incompatibility with standard petroleum fuels [1, 5, 12–16]. It cannot be used as high-quality fuels like gasoline and diesel without any treatments. A number of bio-oil upgrading technologies have been proposed to improve the product properties and to increase the range of possible applications. The majority of the past bio-oil upgrading efforts to date have revolved around catalytic hydrotreating [14, 17–25] and zeolite upgrading [26–31]. These methods suffer from several drawbacks such as catalyst coking and low yields to valuable products [27, 29, 32, 33]. Hence, it is imperative to develop alternative bio-oil upgrading technologies.

A number of studies have been reported dealing with esterification of crude bio-oil by reacting it with alcohol (e.g., methanol) [15, 31, 34–45]. Simultaneous hydrotreating and esterification reactions to upgrade bio-oil have also been investigated [14, 19, 46, 47]. It is anticipated that reactive molecules like organic acids and carbonyl compounds are converted by the reactions with alcohols to esters and acetals as shown in Fig. 30.1a, b, respectively.

It is possible to produce high quality bio-oils by in-line esterification of pyrolysis vapor using ethanol [48]. A reactive distillation based process that uses alcohols like butanol, ethylene glycol and 2-Ethyl hexanol in the presence of solid acid Nafion as a catalyst has been proposed [32]. The heating value and acidity are reported to be considerably improved. In another study [49], it has been revealed that one-pot hydrogenation and esterification improves the bio-oil quality significantly. Pt supported on zeolite was used as a catalyst. Amberlyst-70 is reported to have worked well to facilitate both esterification and acetalization simultaneously. Removal of water is essential to drive the equilibrium in the forward direction. For this purpose molecular sieves have also been proposed to capture the water during the reaction [50]. Though there have been successful attempts to stabilize bio-oil using these techniques on laboratory level, a substantial work still needs to be done on various fronts to scale up this technique. The systematic experimentation on the progress of reaction, effect of different parameters, catalyst reusability etc. is necessary to take this approach forward. It is with this purpose that the present work is undertaken.

In this paper, esterification of bio-oil based on reactive distillation using n-butanol as the reacting alcohol is studied in the presence of Amberlyst-15 as the solid acid catalyst is studied. The bio-oil obtained by this process is examined for the heating value (HHV), water content, viscosity, pH and the shelf life.

$$\text{R-COOH} + \text{R'-OH} \longleftrightarrow \text{R-COOR'} + H_2O$$

Fig. 30.1 Esterification of carboxylic acids

Reactive distillation combines both distillation and chemical reaction into a single unit. In this process, the water in the crude bio-oil as well as the water produced by the various chemical reactions is removed simultaneously by distillation in a single step. It drives the equilibria to completion and is expected to reduce acidity. To prevent excessive evaporation of the reacting alcohol, those alcohols with a boiling point higher than water are chosen. n-Butanol was selected as it is available from renewable resources by fermentation processes [51]. The use of a homogeneous acid catalyst such as sulfuric acid for esterification causes difficulties in recovery after the reaction and produces toxic waste water. Solid acid catalysts such as Amberlyst-15 have been studied as substitutes for sulfuric acid, and have the advantages of being easy to recover and reuse, as well as being compatible with environmental considerations [52–55].

The article is organized as follows: First we describe the experimental setup and procedure. The characterization of the product and the effect of different process parameters on the same are discussed. The catalyst was found to deactivate during the course of the reaction. The factors responsible for deactivation are identified through systematic experiments and characterization of the fresh and used catalyst.

30.2 Experimental Setup and Procedure

30.2.1 Materials

Babul wood vacuum pyrolysis is carried out in an existing pyrolysis unit at IIT-Bombay. The properties of crude bio-oil are summarized in Table 30.1. Dry Methanol (GR grade; 0.02% water max), pyridine-free Karl Fischer solution, sulfuric acid (about 98% GR) and 1-Butanol were supplied by Merck Ltd., India. The catalyst used in the experiments is a commercial strong-acid ion-exchange resin Amberlyst-15 (Dry) obtained from Rohm and Hass, India.

Table 30.1 Properties of crude bio-oil

Physical properties	Values
Moisture content (wt%)	26.36
pH	2.80
Density (kg m^{-3})	1.08
Ash (wt%)	0.03
HHV (MJ kg^{-1})	22.20
Viscosity (cP) at T = 40 °C	73.62
Elemental composition (wt%)	
Carbon	50.92
Hydrogen	8.27
Oxygen (by difference)	38.57
Nitrogen	2.23

30.2.2 Experimental Procedure

The reactive-distillation setup mainly consists of a three-neck round bottom glass flask (250 ml) equipped with stirrer and Dean-stark apparatus as shown in Fig. 30.2. The temperature in the reactor was measured using a thermometer and boil-up is maintained with the help of a heating mantle.

Typically, 50 ml of bio-oil and 50 ml of 1-butanol are mixed and mixture is filtered over a filter paper of 11 μm by applying vacuum. The filtrate thus obtained is then centrifuged for 30 min at a rate of 2420 RPM. The clear liquid is separated and charged into the reactor vessel. The reactor mixture is heated to the boiling temperature and a certain boilup is maintained. Subsequently, Amberlyst-15 (10 wt % of bio-oil) is added in the reaction mixture. The time at which the first drop of distillate appears in the condenser is considered as zero reaction time. A reaction is typically performed over a period of 120–150 min.

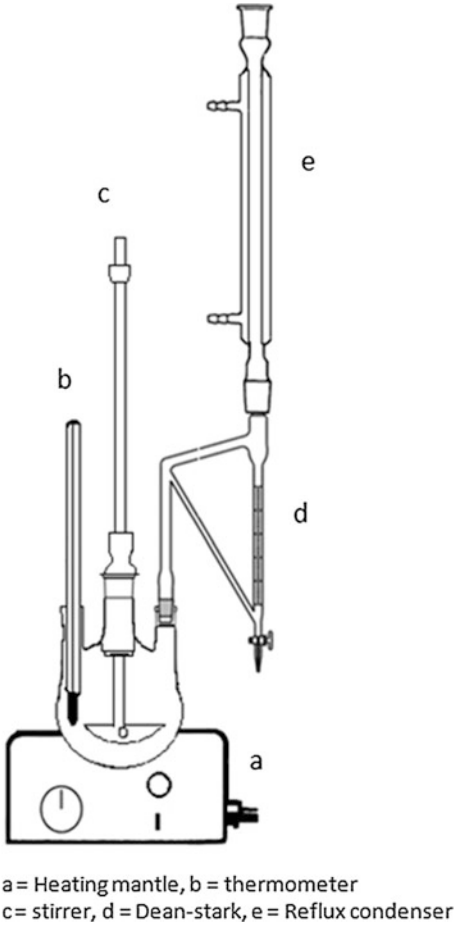

Fig. 30.2 Batch reactive distillation set-up

30.2.3 Catalyst Characterization

Thermogravimetric analysis of Amberlyst-15 is carried out over a temperature range of 120–1000 °C at rate of 2 °C/min and then kept constant for 10 min to ensure the completion of analysis and under flowing N_2 atmosphere with gas flow rate was 150 ml/min. Surface area of the catalyst is determined by a standard BET (Nitrogen adsorption at −195 °C) technique on an automated adsorption apparatus (ASAP 2020 V3.01 H, Micromeritics, USA), and surface area of fresh Amberlyst-15 was found to have 43.9 m^2/g.

30.2.4 Bio-oil Characterization

As Bio-oil is a complex matrix with more than 400 different chemical compounds present, it is difficult to evaluate the catalyst performance based on the conversions of individual components [7, 32]. However, physical properties of esterified bio-oil can be accurately quantified by various techniques. They include, moisture content by means of a Karl-Fischer titration, heating value from elemental analysis, viscosity using Cannon-Fenske viscometer tube and product identification and composition by Gas chromatography-Mass spectrometer (GC-MS).

Bio-oil distillate is analyzed qualitatively by GC-MS and quantitatively by GC-Flame ionization detector. The separation was achieved on 30 m long BP-5 column (i.d. = 0.32 mm) and film thickness of 0.25 μm. The GC oven temperature was set initially at 50 °C and then raised to 200 °C at a rate of 10 °C/min. The injector split ratio was set at 50:1, and hydrogen is used as a carrier gas with a flow rate of 0.5 ml/min. The moisture content of the crude bio-oil was determined using a Karl-Fischer titrator (VEEGO/MATIC-D). Standard method ASTM E 203 is used to measure the moisture content of crude bio-oil as well as esterified bio-oil.

30.3 Result and Discussion

30.3.1 Bio-oil Distillate

Table 30.2 Shows different components distilled out over a temperature range of 370–378 K with their weight percentages. Some of them are formed due to chemical reactions shown in Fig. 30.1. A significant amount of water is present in the bio-oil and in addition, small amount is formed in the reactions; much of it is removed using Dean-stark apparatus. This analysis shows that desired reactions proceed in forward direction and organic acids such as formic acid, acetic acid and propanoic acid which are responsible for high acidity of crude bio-oil are converted to respective 1-butyl esters. Low boiling point compounds such as methanol are

Table 30.2 Different components in distillate of Bio-oil

Sr. no	Component name	wt%
1	Methanol	0.52
2	Methyl acetate	0.26
3	1-butanol	79.83
4	1-butyl formate	7.70
5	1-butyl acetate	11.37
6	Furfural	0.19
7	di-butyl ether	0.17
8	1-butyl propionate	0.07

distilled out at this reaction temperature. di-Butyl ether is also formed in the reaction and organic layer is recycled back into the reactor vessel using Dean-stark arrangement as shown in Fig. 30.2. Small amount of furfural also appears in distillate.

30.3.2 *Esterified Bio-oil*

The physical properties of bio-oil such as kinematic viscosity, pH, HHV and water content are evaluated before and after the alcohol treatment. Physical appearance (e.g., color) of the products was close to that of the original bio-oil. However, the odor changed dramatically from smoky pungent to banana like. This change is due to the formation of butyl esters of organic acids having a very typical sweet, banana-like odor.

The experiments are carried out using 1wt% H_2SO_4 and without catalyst to compare the performance of solid acid catalyst in terms of the conversion of acids to esters. For 1wt% H_2SO_4, ester formation is 6.15 wt%. It would be possible to further enhance the conversion however by increasing the sulfuric acid concentration. However, as we know large amounts of sulfuric acid, result in problems such as difficulty in its separation and corrosion. Figure 30.3 shows performance of different catalysts in the production of 1-butyl acetate compared to heterogeneous catalyst Amberlyst-15. Without catalyst, reaction yield is very poor and 1-butyl acetate produced is as low as 1.76 wt%.

Esterified bio-oil using heterogonous and homogeneous catalyst is compared using the characteristics properties of bio-oil.

Figure 30.4 shows that the water content of the treated bio-oil reduces from 26.36 to 4.29 wt%. It can be further reduced by prolong heating to high temperatures but high temperatures causes polymerization reactions; moreover, catalyst thermal stability limit is 393 K [52–54]. Esterified bio-oil with sulfuric acid also shows significant reduction in the moisture content but sulfuric acid. We have found that the reactions take place even in the absence of catalyst though the extent is significantly lower than that in the presence of Amberlyst 15.

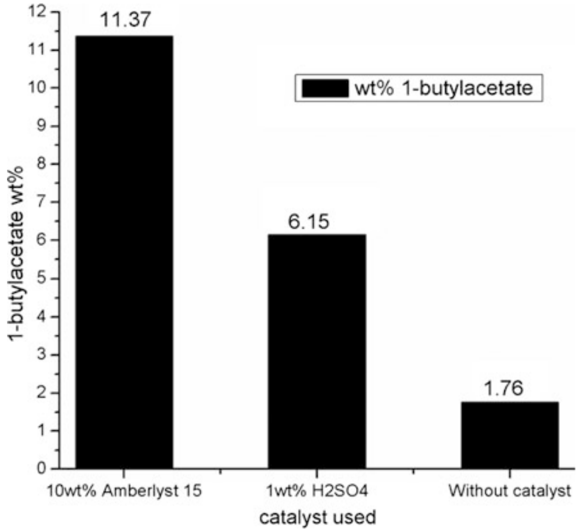

Fig. 30.3 Formation of 1-butyl acetate using different catalysts

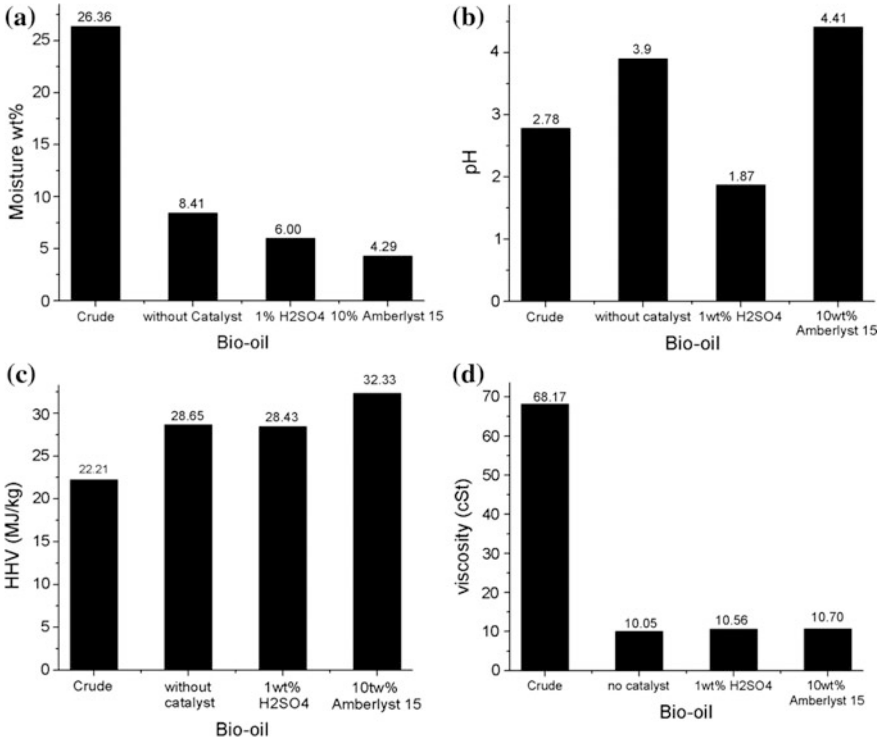

Fig. 30.4 Esterified Bio-oil product properties. **a** Moisture wt%, **b** pH Value, **c** HHV(MJ/kg), **d** viscosity (cSt)

The pH of the treated Bio-oil with sulfuric acid drops from 2.78 to 1.87 while with Amberlyst-15, it shows an improvement i.e., a rise from 2.78 to 4.41. The pH value of bio-oil products obtained without catalyst, improved to 3.9 as shown in the Fig. 30.4. The improvement in the pH value of the treated bio-oil with different catalysts is due to the dilution effect of 1-butanol as well as the occurrence of esterification reactions catalyzed by organic acids present in bio-oil.

30.3.3 Higher Heating Value

Higher heating value (HHV) of the crude Bio-oil is 22.21 MJ/kg, it is determined based on the Elemental analysis [32] of crude bio-oil and values are tabulated in Table 30.3. Bomb calorimeter could not be used to determine HHV due to high moisture content of the crude bio-oil. Hence for consistency, HHV of the esterified bio-oil is also determined by elemental analysis. It is found to increase to 32.33 MJ/kg after treating with 1-butanol in the presence of Amberlyst-15. Further, in the presence of sulfuric acid HHV is found to be 28.43 MJ/kg and that without catalyst it is 28.65 MJ/kg as shown in Fig. 30.4. Reasons for improving the HHV of bio-oil is water reduction in the product bio-oil as well as presence of large amount of 1-butanol (HHV: 37.5 MJ/kg).

30.3.4 Viscosity

Figure 30.4 shows the kinematic viscosity of different esterified bio-oils prepared using different methods. The kinematic viscosity of the crude bio-oil (moisture 26.36 wt%) is measured using Cannon-Fenske viscometer tube of size 300 (calibration constant is 0.25) at 40 °C and it is 68.17 cSt. The same after alcohol treatment in the presence of Amberlyst-15 is reduced to 10.7 cSt. This improvement in the viscosity is due to the dilution of 1-butanol. In the presence of sulfuric acid, viscosity is reduced to 10.56 cSt and without catalyst treatment viscosity reduced to 10.05 cSt.

Table 30.3 Elemental analysis of Bio-oil

Elements (wt%)	Crude bio-oil	No catalyst	1wt% H_2SO_4	10wt% Amberlyst-15
Carbon	50.92	56.83	55.05	60.93
Hydrogen	8.27	10.34	10.75	11.32
Nitrogen	2.23	2.39	2.55	2.16
Oxygen (by difference)	38.57	30.43	31.63	25.58
HHV (MJ/kg)	22.21	28.65	28.43	32.33

30.4 Catalyst Activity

To check the activity of the catalyst, the reaction is performed under otherwise similar conditions in the presence of the catalyst washed with isopropyl alcohol repeatedly and dried under vacuum for 8 h at 80 °C. The formation of 1-butyl ester is reduced from 11.37 to 7.32 wt%, which shows a decrease in the activity of the catalyst.

To identify the cause of deactivation, Amberlyst-15 was characterized for the surface area using BET apparatus; specific surface area of catalyst dropped from 43.97 to 16.94 m^2/g, in two reuses as shown in Fig. 30.5a, which is probably due to surface deposition and blockage of pores. To confirm this deposition TG Analysis of the re-used Amberlystp-15 is carried out and compared with the fresh catalyst. The weight loss of the used Amberlyst-15 is found to be more than fresh Amberlyst-15 as shown in Fig. 30.5b. It may be concluded that that used Amberlyst-15 suffers from surface depositions which leads to surface blockage and active sites of the catalyst.

An overview of the product properties of the esterified bio-oil obtained using Amberlyst-15, H_2SO_4 and no catalyst are summarized in Table 30.4 and compared

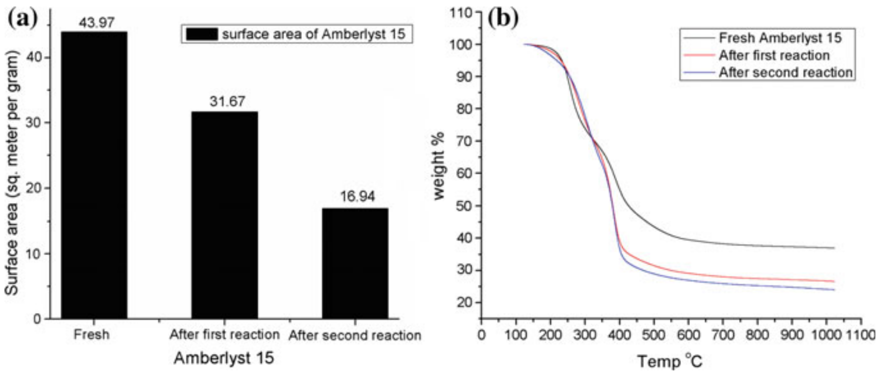

Fig. 30.5 **a** Surface area of Amberlyst-15. **b** Thermogravimetric profile of Amberlyst-15

Table 30.4 Product Properties of crude bio-oil, esterified bio-oil, and diesel

Physical properties	Crude bio-oil	Esterified bio-oil	Esterified bio-oil	Esterified bio-oil	Diesel
Catalyst	–	Amberlyst-15	H_2SO_4	No catalyst	–
Kinetic viscosity at 40 °C cSt	68.17	11.27	10.56	10.05	1.9–6.0
Water content wt%	26.36	4.29	6.00	8.41	<0.05 vol.%
Oxygen wt%	38.57	25.58	31.63	30.43	0.0
pH	2.78	4.41	1.87	3.90	7.00
HHV MJ kg^{-1}	22.21	32.33	28.43	28.65	44.8

with petroleum diesel. Some improvements are clearly shown when using Amberlyst-15. For example, the pH value improved considerably and the water content is reduced to 4.29%, leading to a considerable improvement of the HHV to 32.33 MJ kg^{-1}.

30.5 Conclusions

Esterification of wood pyrolysis oil with high boiling alcohol like n-butanol in the presence of Amberlyst-15 is investigated. In this process, using reactive distillation of bio-oil water content and acidity of bio-oil reduced significantly. With this catalyst, a subsequent neutralization step after treatment is avoided, however, it deactivates due to deposition of carbonaceous material formed by certain compounds present in the bio-oil. Systematic experimental studies will be required to investigate the cause of deactivation.

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