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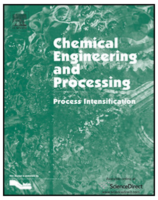

# Stabilization of pyrolysis oil: Comparison of reactive distillation and reactive chromatography

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ABSTRACT

The present study, evaluates the applicability of reactive distillation and reactive chromatography for stabilization of bio-oil, obtained from pyrolysis of wood. Bio-oil, along with several oxygenated organic compounds, contains substantial amounts of carboxylic acids (e.g., acetic acid, 5–10%). The presence of acids results in a shorter shelf life of bio-oil, as it catalyzes condensation reactions of furfural-like components leading to an increase in viscosity over a time period. Thus, we investigate the ability of multifunctional reactor for stabilization of bio-oil through esterification of acid with suitable alcohol in the presence of ion-exchange resin catalyst. Reactive distillation is performed at higher a temperature which is dictated by the bubble point of the mixture, reactive chromatography allows one to perform reaction at relatively low temperatures and with lower alcohols. It results in an improvement in the characteristic properties of bio-oil, thereby increasing the shelf life. The main limitation of this approach is that the catalyst used for esterification also catalyzes simultaneous polymerization of furfural-like components which deactivate the catalyst. Deactivation of Amberlyst-15 with ethanol after 20 h of continuous run in a fixed-bed chromatographic-reactor was found to be less compared to RD making RC a promising candidate for this particular application.

## 1. Introduction

With the fast depletion of petroleum reserves, renewable resources like biomass are acquiring great significance. Bio-oil obtained from fast pyrolysis of waste biomass has a potential to produce valued chemicals and clean, renewable liquid fuels in future because waste biomass is fast growing and abundant [1,2]. Bio-oil has a higher energy density than the raw biomass feedstock. However, bio-oil has some inferior properties, such as its low heating value, poor volatility, high oxygen content, water content, acidic pH values, strong unpleasant odor, and instability and incompatibility with standard petroleum fuels [2–5]. Thus, without further treatment, it cannot be used to replace high-quality fuels like gasoline and diesel.

Several technologies have been proposed to improve the properties of bio-oil and to increase the range of its applications. Most of such efforts to date, have revolved around zeolite cracking [6–9], hydrodeoxygenation [10–14], steam reforming [15,16], esterification [17,19], and integrated catalytic processing such as hydro-processing with zeolite catalysis [13]. Catalytic cracking offers significant processing and economic advantages over the other methods, but bio-oil cracking produces extensive tars and coking of catalyst takes places. Hydrodeoxygenation can increase energy content and stability of bio-oil, however, it operates at high pressures and consumes substantial amount of hydrogen. Steam reforming of bio-oil produces syngas, which can be converted further into a range of fuels. However, high temperatures are needed and extensive coke deposits are formed in the reactor and it must be gasified. One possible alternative is to stabilize bio-oil and use it as a liquid fuel. The main cause of instability of bio-oil is condensation and polymerization of furfural-like components that prevail under acidic conditions due to the presence of carboxylic acids [20]. Esterification with alcohols can convert carboxylic acids in bio-oil to esters and reduce the extent of polymerization. Furthermore, blending with appropriate amounts of the same alcohol reduces pH and also the viscosity. There have been successful attempts to stabilize bio-oil using these techniques at a laboratory level [21–23]. However, to the best of our knowledge, substantial work is still necessary to investigate the engineering aspects involved in scaling up these attempts. The present work is therefore undertaken to throw a light on these problems.

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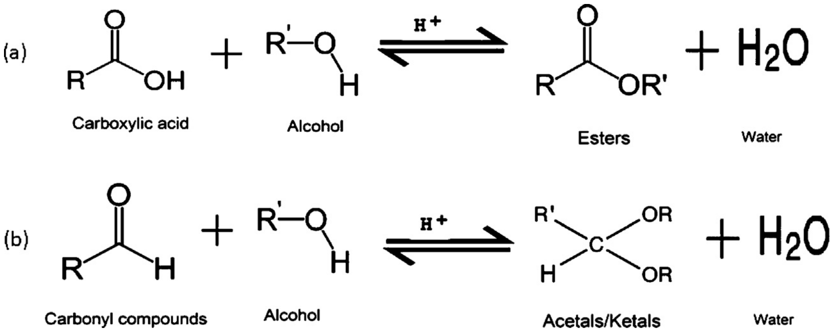

**Fig. 1.** (a) Esterification of carboxylic acids. (b) Acetalization/ketalization of carbonyl compounds.

Esterification, being a reversible reaction (Fig. 1(a)), can be expedited by simultaneous removal of water formed during the course of reaction. Aldehydes and ketones present in bio-oil, if any, are converted to the corresponding acetals and ketals (Fig. 1(b)) [24]. Multifunctional reactor that combines reaction and separation in a single unit is a promising alternative to the conventional approach of reaction-followed-by-separation. Reactive distillation (RD) has been widely used for these reactions [25–30] and in our previous work [31], we explored the possibility of using the same for the stabilization of bio-oil by a reaction with *n*-butanol in batch mode. In this case, the water formed in the reaction escapes from the reactor easily as it has a tendency to form a minimum-boiling heterogeneous azeotrope with *n*-butanol and product *n*-butyl acetate. The vapors, upon condensation, form two liquid phases thereby facilitating separation water. It makes *n*-butanol a better choice against the lighter alcohols such as methanol/ethanol. However, the major problem in this route is the simultaneous deactivation of catalyst due to condensation/polymerization of furfural-like compounds in bio-oil at the corresponding operating temperature (95 °C). In a typical reactive batch rectification type of operation, reaction takes place in the reboiler in which heavy molecules responsible for the deactivation of catalyst also accumulate over a period. It is expected that the use of continuous reactive distillation would help separate the heavy boiling deactivating compounds from the catalytic zone, during the course of reaction thereby avoiding or minimizing deactivation that is otherwise observed in conventional reactors. Furthermore, use of ethanol and methanol in RD may also be investigated. Such an application of RD to avoid catalyst deactivation has been explored for hydrodesulphurization of diesel from the petroleum fraction in the past [32]. In this work, we make an attempt to examine the potential of RD for bio-oil stabilization using methanol, ethanol and *n*-butanol.

Chromatographic reactor (RC) is another multifunctional reactor that combines chromatography with reaction and offers flexibility in operating temperature in case of thermolabile chemical species and catalyst. To date, various heterogeneous reactions like esterification [33–36], etherification [37], acetalization [38], isomerization [39,40], etc., have been successfully studied in chromatographic reactors.

In RC, the selection of packing material is an important factor as it should not only act as a catalyst for the reaction but also adsorb one of the products, selectively. Synthetic bio-oil mixture flows over packing material such that esterification and separation of products occur simultaneously. Here, we target the conversion of acid by reacting it with alcohol and choose an adsorbent such that it has more affinity for water and less affinity for ester. Thus the ester elutes first, and water with higher affinity lags behind thereby shifting the reaction in the forward direction. The reaction rates and relative affinities of the components towards the packing material together, decide the feasibility of RC for a given reaction. Fixed bed chromatographic reactor (FBCR) can be conveniently used to evaluate feasibility of RC for a given reaction. The performance of FBCR is analysed using the breakthrough curves. Once the feasibility is proven, the reaction can be conveniently conducted in a continuous mode reactor like simulated moving bed reactor (SMBR) [38].

Another advantage of RC is that, unlike RD, the operating temperature is not limited by the vapor–liquid equilibrium thereby providing a greater temperature window to minimize deactivation. Furthermore, one can conveniently use lighter and more reactive alcohols such as methanol/ethanol in this case. The choice of methanol/ethanol as the reacting alcohol is based on the fact that they can be produced economically and from bio-sources. Furthermore, being reactive, the reactions take place at relatively low temperatures thereby suppressing the side reactions and hence the catalyst deactivation observed otherwise at high temperature [31]. In this work, we perform systematic experiments to evaluate applicability of RC for this application and compare its potential with that of RD. Since RC is found to be a promising option, we generate relevant data on kinetics and adsorption isotherm to develop a reactor model and validate it experimentally.

The rest of the article is organized as follows: first we describe the analytical methods, apparatus and operating procedure used for reactive distillation and reactive chromatography. The applicability of RD is then discussed through the experimental results on reaction conversion and extent of catalyst deactivation. Systematic investigation of RC needs determination of reaction kinetics and adsorption isotherm by performing relevant experiments and estimating the corresponding parameters. The reactive breakthrough curves are then presented to show the feasibility of RC. The conditions to minimize deactivation are obtained through experiments. Both kinetics and isotherm are used to predict reactive breakthrough curves in RC using appropriate reactor model, and the results are compared with the experimental data to form a basis for the design of large-scale continuous process.

## 2. Experimental work

### 2.1. Materials

Methanol (GR grade; 0.02% water), acetic acid (glacial, 99.8%), phenol (GR grade, 99.8%), synthesis-grade ethyl acetate (99.5%), ethanol (99% pure) and *n*-butanol (GR grade 99.8%) were obtained from Merck Ltd., India. Furfural (AR grade 99%) and guaiacol (LR grade, 99%) were obtained from S-D Fine Chemicals Ltd., India. *o*-Cresol and cyclopentanone were supplied by Spectrochem Pvt., Ltd., India. The catalyst used in the present work was commercial strong-acid ion-exchange resin, Amberlyst-15 (dry), obtained from Rohm and Hass, India. In this work a synthetic bio-oil was used in all the experimental studies.