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### Review

## Upgrading of bio-oil via acid-catalyzed reactions in alcohols – A mini review

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### ABSTRACT

Bio-oil is a condensable liquid produced from the pyrolysis of biomass, which can be upgraded to biofuels. Bio-oil is corrosive as it contains significant amounts of carboxylic acids, creating difficulties in handling of bio-oil and applications of bio-oil. Acid-treatment of bio-oil in alcohols is an upgrading method to transform the carboxylic acids in bio-oil into neutral esters. This study reviewed the recent progress in the research about the acid-catalyzed conversion of bio-oil in alcohols. The various catalytic processes for the acid treatment of bio-oil and the reaction network of some individual components of bio-oil during the upgrading were focused. The interactions among the main components of bio-oil during the acid-treatments were also discussed.

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### 1. Introduction

Biomass is a renewable and abundantly available feedstock for the production of biofuels and chemicals [1]. Pyrolysis is a thermal method for the conversion of solid biomass in absence of oxygen into a condensable liquid named as pyrolysis oil or bio-oil [2]. Bio-oil is a mixture of hundreds of chemicals [3]. It has some deleterious properties such as a high viscosity, a high water content, a high instability and a high corrosiveness [4,5]. These undesirable properties make the direct use of bio-oil as the fuel for transportation difficult.

Although the composition of bio-oil depends on the feedstock and the pyrolysis conditions [6–8], majority of these organic compounds have the oxygen-containing functionalities. This leads to a low heating value and a high instability of bio-oil [9,10]. Bio-oil thus has to be stabilized and be upgraded to improve its properties for the use as the fuel for vehicles [11–13].

Among the various oxygen-containing organics in bio-oil, the carboxylic acids received particular attention as they are the main origin of the corrosiveness of bio-oil. Moreover, the carboxylic acids are also the catalysts for the polymerization of bio-oil [14–16]. Esterification is effective for the transformation of the carboxylic acids in bio-oil into neutral esters via the acid treatment of bio-oil in alcohols. Esterification of bio-oil was generally performed at the temperature under 250 °C, as at higher reaction temperature (i.e. 400 °C) cracking of the components in bio-oil became dominant [17,18]. Under the conditions of esterification, not only the carboxylic acids but also many other components

such as aldehydes, sugars, furans and some phenolics are converted, via distinct reaction routes. These reactions together drastically modify the composition of bio-oil, improve the stability and alleviate the polymerization of bio-oil during the further hydrotreatment [19].

Acid catalyzed conversion of bio-oil in alcohols has significant importance in biorefinery. It significantly changes the composition of the bio-oil produced from upstream pyrolysis and modifies the reaction behaviours of bio-oil in the downstream hydrotreatment. Reaction temperature significantly affects the conversion routes of most of the components in bio-oil. Generally, below, esterification is predominant pathways for the acid-treatment of bio-oil in alcohols. While above 400 °C, the components of bio-oil mainly undergo catalytic cracking.

Because of the unique importance, it is necessary to revisit and review the research work dealing with esterification of bio-oil. Ciddor et al. have recently reviewed the catalytic esterification of bio-oil but with a special focus on catalysts [20]. Little attention has been paid on the reaction network, which is the key to understand how esterification impacts the composition of bio-oil. This review focuses on the reaction pathways of the individual components of bio-oil including carboxylic acids, aldehydes, furans, sugars, phenolics, terpenoids, N-containing organics and metal species during esterification. Other aspects of esterification such as the process employed (i.e. inline esterification, esterification in olefins/alcohols, esterification coupled with pre-oxidation or hydrogenation, reactive distillation) will also be discussed. The catalysts used in bio-oil esterification will be briefly mentioned.

The work from the authors of this study will be biased, especially in the sections about the reaction network during bio-oil esterification. Some other relevant review papers were also mentioned here for reference. Mohan et al. have reviewed the progress in pyrolysis of biomass

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for bio-oil production [21]. Asadieraghi et al. [22], Tan et al. [23], and Park et al. [24] have reviewed the catalytic pyrolysis of biomass. Chen et al. have reviewed the research progresses in stabilisation of bio-oil during storage [25]. Hydrotreatment of bio-oil was reviewed by Elliott in 2007 [26] and more recently by Wang et al. [27].

## 2. Esterification of the bio-oil derived model compounds

Acid catalyst is generally required for esterification of the carboxylic acids in bio-oil. Under the conditions of esterification, the acid catalyst could also catalyze a number of other reactions including transesterification, acetalization, etherification, oligomerization, aldol condensation, dehydration/decomposition of sugars/furans and polymerization reactions. These reactions together make the reaction network in esterification of bio-oil very complex. In order to understand the reaction behaviour of a specific component during the acid treatment, it is much easier to start the investigation by a model-compound approach. Besides, model-compound experiment is also commonly performed to evaluate performance of catalysts [28–33] or the processes for esterification of bio-oil [34–37]. As shown in Table 1, the esterification of the different acids including acetic acid, fatty acids and levulinic acid were investigated. These acids all can be effectively esterified but their relative reactivities towards esterification could not be compared here due to the different catalysts and reaction conditions used.

Instead of esterification of the acids in alcohols, esterification of the carboxylic acid in phenolics has also been attempted. Milina et al. investigated the esterification of acetic acid with o-cresol (Fig. 1) [33]. This proposed esterification method has significant importance, as the phenolics are one of the most abundant components in bio-oil. The use of the phenolic compounds to esterify the carboxylic acids in bio-oil does not require external alcohols, which has an unprecedented advantage. However, the conversion of acetic acid could reach only ca. 60% at 200 °C in o-cresol. At this high temperature, polymerization reactions also took place. The conversion of acetic acid was not high enough over the catalysts tested in the study. It has not been understood yet about the activity of other catalysts for this reaction. More effort (i.e. developing more active catalysts) is required to further develop this method.

The carboxylic acids in bio-oil could also react with the alcohols formed from the in-situ hydrogenation of the aldehydes in bio-oil. Tang et al. developed a one-step hydrogenation/esterification method

to convert the aldehydes into alcohols via an initial hydrogenation step [35]. The carboxylic acids then reacted with the produced alcohols to form esters via esterification (Fig. 2) [35]. Using the same philosophy, the hydrogenation/esterification of furfural or other aldehydes with acetic acid were also investigated [36]. The main advantage of this method is that there is no need to use external alcohols for esterification. However, the amount of aldehydes in bio-oil may not be abundant enough to produce enough alcohols to esterify the carboxylic acids in bio-oil. The reactivity of the produced alcohols with the acids also needs to be considered to optimize the process to maximize the output of this method.

Aldehydes are an important component of bio-oil. Lohitharn and Shanks found that, during esterification, acetaldehyde affected the conversion of acetic acid, especially at the low reaction temperatures (50–70 °C) [32]. The acetalization and esterification took place simultaneously and competed for the same acidic sites, affecting the conversion of each other. Higher reaction temperature (100 °C) enhanced the reaction rates for both the esterification and acetalization, and the competition became insignificant. In bio-oil, not only aldehydes but also many other reactants such as furans, sugars and phenolics compete for the same acidic sites during the acid treatment of bio-oil. This would also affect the conversion of carboxylic acids, which, however, has not been fully understood yet.

Except the conversion of aldehydes via acetalization, Ye et al. investigated the alkylation of acetaldehyde with 2-methylfuran (Fig. 3) [31]. The 2,2'-ethylidenebis(5-methylfuran) formed via the alkylation method are more stable than the corresponding acetal. However, the alkylation as a method for the conversion of aldehydes has not been confirmed yet in bio-oil. Many compounds in bio-oil could be converted via the alkylation reactions and they would possibly compete with alkylation of acetaldehyde.

## 3. Esterification of bio-oil via various methods

### 3.1. Esterification of bio-oil in alcohols

Esterification of bio-oil in alcohols is a primary method to deal with the corrosiveness of bio-oil. The amounts of alcohols in bio-oil are generally not able to esterify the carboxylic acids effectively. Addition of alcohols to bio-oil is adopted to perform the esterification in many research works, as shown in Table 2 [38–71]. The alcohols used include

**Table 1**  
Esterification of the model compounds in bio-oil.

Entry	Methods	Reactants	Solvent	Catalyst	T (°C)	Ref
1	Esterification	Acetic acid	Methanol	SO <sub>3</sub> H-SBA-15/Pr(10)	50	[28]
	<i>Functionalization of SO<sub>3</sub>H-SBA-15 with hydrophobic propyl groups effectively increased the water tolerance in esterification.</i>					
2	Esterification	Fatty acids	Methanol	Macroporous cation exchange resin	70	[29]
	<i>Macroporous resin performs better than gel-type resin but shows physical instability.</i>					
3	Esterification	Levulinic acid	Ethanol	ZrO <sub>2</sub> -TiO <sub>2</sub> -SO <sub>3</sub> H	110	[30]
	<i>The catalyst showed high activity for the esterification of levulinic acid.</i>					
4	Esterification	Acetic acid, acetaldehyde	1-Butanol	Silica sulfuric acid	140	[31]
	<i>The decomposition of acetals was successfully resolved by an alkylation reaction of acetaldehyde.</i>					
5	Esterification	Acetic acid, acetaldehyde	Ethanol	SBA-15-SO <sub>3</sub> H	100	[32]
	<i>Aldehyde mainly affects acid conversion at the lower reaction temperatures via competition.</i>					
6	Esterification	Acetic acid	o-Cresol	ZSM-5, mordenite ...	220	[33]
	<i>Large-pore zeolites were more active for esterification than medium-pore zeolites. High temperature was required to catalyze the esterification of phenolic alcohols, which also promoted coke formation.</i>					
7	Esterification	Phenol, acetic acid, acetaldehyde/hydroxyacetone/glucose	1-Octene/1-butanol	Dowex50WX2, Amberlyst15 Amberlyst36	120	[34]
	<i>Upgrading of bio-oil in olefin/alcohol involves phenol alkylation, olefin hydration, esterification, etherification, acetal formation, olefin isomerization and oligomerization and intermolecular aldol condensation.</i>					
8	Esterification/hydrogenation	Acetaldehyde, acetic acid, butyl aldehyde	Methanol	Pt/Al <sub>2</sub> (SiO <sub>3</sub> ) <sub>3</sub> Pt/HZSM-5	150	[35]
	<i>The catalysts with large pore size and strong acid sites may be beneficial for the one-step hydrogenation/esterification.</i>					
9	Esterification/hydrogenation	Furfural, acetic acid		Pd/Al-SBA-15	150	[36]
	<i>Synergistic effect between the metal sites and the acid sites exist.</i>					
10	Esterification/hydrogenation	Acetic acid, acetaldehyde		Pt/SBA15-PrSO <sub>3</sub> H	150	[37]
	<i>The bifunctional Pt/SBA15-PrSO<sub>3</sub>H catalyst is much more active than SBA15-PrSO<sub>3</sub>H catalyst.</i>					

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