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Acid-catalyzed liquid-phase alkylation of phenol with branched and linear olefin isomers

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ABSTRACT

Alkylation of phenolic compounds with olefins is an important industrial reaction to increase the chemical stability of bio-oil. In this study, the liquid-phase alkylation of phenol with linear (1-octene) and branched (diisobutylene) olefins was studied, in a batch reactor using homogeneous (sulfuric acid) and heterogeneous (Amberlyst-15) acid catalysts. Conversion and selectivity trends were compared and the effects of different operational conditions (temperature, phenol/olefin molar ratio and catalyst content) were evaluated employing factorial experimental design. The Amberlyst-15 solids acid resin was characterized by nitrogen physisorption and Brønsted acid sites titration. The heterogeneous catalyst showed satisfactory conversions with both olefins, albeit being less active than sulfuric acid. Higher conversions were obtained with diisobutylene than with 1-octene. C-alkylation was dominant in the diisobutylene reaction, including some product formation resulting from fragmentation of the diisobutylene olefin. However, mainly O-alkylation was observed under mild reaction conditions in the 1-octene reaction. Factorial experimental design showed that temperature was the variable that most influenced the conversion and selectivity trends, and the highest yields of di- and tri-alkylated products were obtained at elevated temperatures. A mechanistic model was proposed for both reactions.

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1. Introduction

Bio-oil produced by pyrolysis of biomass is a promising renewable source for production of both fuels and chemicals. [1,2] Czernik and Bridgwater [3] describe bio-oil as a multicomponent mixture containing molecules of various sizes, principally derived from depolymerization and fragmentation of the three main constituents of biomass: cellulose, hemicellulose and lignin. Thermal

pyrolysis of biomass yields the liquid bio-oil product with a typical oxygen content of 35–40% by weight. Various oxygen-containing organic functional groups can be present in bio-oil, with ratios depending on the type of biomass used and harshness of the reaction conditions, e.g. temperature, treatment time and heating profile. The main compounds in different bio-oils were reported as phenols, carboxylic acids, alcohols, ketones, aldehydes, ethers, esters, amines, furans, aliphatic and aromatic hydrocarbons and carbohydrate-derived oxygenates [1–5]. One of the most abundant chemical groups in bio-oil are phenols [6,7] which can be used as feedstock in phenol-formaldehyde resins [8].

The presence of oxygenated compounds is directly responsible for several undesired characteristics of bio-oil. This especially includes its use as fuel compared to diesel and fuel oil, presenting low calorific value, poor volatility, high viscosity, high

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acidity and cold flow problems. Additionally, oxygenates may undergo polymerization during storage, resulting in increased viscosity and average molar mass, phase separation, reduced thermal stability and volatility. To improve the properties of bio-oil, upgrading processes are essential, which focusing on decreasing the oxygen content and producing more stable compounds through hydrotreating, catalytic cracking over zeolites and steam reforming [2,6].

Among the upgrading processes, alkylation of phenolic compounds with olefins or alcohols is a promising alternative method to improve the chemical stability of the bio-oil. The transformation of unstable oxygenated compounds into stable compounds can typically be done under milder reaction conditions than other upgrading processes. During the alkylation reaction, alkyl or aryl groups are introduced to the phenol molecule. When insertion occurs to a carbon atom in the aromatic ring, this is called C-alkylation and alkylphenols are produced, which are widely used as petroleum additives, food antioxidants, polymer heat stabilizers and as raw materials for phenolic resins, surface coatings, fungicides, cosmetics and as pharmaceuticals [9,10]. Depending on the reaction conditions, *ortho*-alkyl, *meta*-alkyl and *para*-alkylphenols and also di- and tri-alkylated compounds can be produced [10]. On the other hand, when alkyl insertion occurs through the oxygen atom of the hydroxyl group, it is called O-alkylation. This reaction produces aryl alkyl ethers, which also serve important industrial applications, such as for starting material in the production of agrochemicals and dyes, as stabilizers for plastics and antioxidants for oils and grease [11].

The alkyl group for alkylation may come from different compounds, especially alcohols and olefins. The most reported alkylating agent is *tert*-butyl alcohol [10,12–17], but other alcohols such as methanol, ethanol, *n*-propanol and *n*-butanol have also been reported [11,18,19]. Regarding olefins as alkylating agent, 1-octene is the most studied compound [20–22], but isobutylene [23,24] and cyclohexene [25,26] have also been reported. Typically, alkylation is an acid-catalyzed reaction and although traditional homogeneous catalysts such as HF, H₂SO₄, H₃PO₄, AlCl₃ and BF₃ [9,12] and ionic liquids [10,12,13] have been employed, heterogeneous catalytic processes are industrially preferred. The use of several solid acid catalysts has been reported, such as cation-exchange resins [9,22,24], zeolites [14–16,18–21,23,26], functionalized silica [11,17], mixed oxides like WO₃/ZrO₂ [24], supported AlPO₄ and BF₃ [25] and heteropoly acids.

Although several studies were reported on phenol alkylation, none of those directly compared branched and linear olefins. To our knowledge, no study has yet been reported on phenol alkylation with diisobutylene, which has the advantage over isobutylene that it is liquid at room temperature and has a longer chain, facilitating liquid-phase reactions. Moreover, the resulting alkylated products will have more carbon atoms attached to the aromatic ring and consequently a lower polarity. This makes the alkylated compounds promising for applications in apolar media, e.g. as petroleum-derived (gasoline, lubricant) additives.

The objective of this study is to compare the performance of a commercial solid acid catalyst (Amberlyst-15) against a homogeneous catalyst (sulfuric acid) in the liquid-phase alkylation of phenol with two C₈ olefin isomers, namely a linear (1-octene) and a branched (diisobutylene) isomer. The effects of different operational variables (temperature, catalyst content and reactants molar ratio) on the phenol conversion and products distribution will be evaluated. A mechanistic model will be proposed. Herein, the focus lies on the diisobutylene reaction, which to our knowledge, has not yet been reported in literature.

2. Material and methods

2.1. Catalysts and chemicals

The commercial solid acid resin Amberlyst-15 (A-15; Fluka Analytical) used in our investigation was obtained in the form of spherical beads. It was macerated and dried at 120 °C for 3 h before use. Sulfuric acid (H₂SO₄; Chemis, 95–98%) was used without dilution, as the homogeneous catalyst.

Liquefied phenol (Sigma-Aldrich, ≥89%) was used as the model reactant representing phenolic compounds in bio-oil. Two C₈ isomers, namely linear 1-octene (Sigma-Aldrich, ≥98%) and branched diisobutylene (Sigma-Aldrich, ≥90%), were used as olefins for alkylation.

2.2. Catalyst characterization

The number of Brønsted acid sites was estimated by an acid-base titration technique described by Lopez et al. [27]. The catalyst (approximately 200 mg) was added to a NaCl_(aq) solution (10 mL; 3.42 M) and then kept under stirring for 30 h at 28 °C. After an ion exchange (H⁺ by Na⁺) process, the suspension was filtered off and titrated with a NaOH_(aq) solution (0.05 N), until pH 7 was reached.

The catalysts total specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The nitrogen physisorption measurement was performed on a Micromeritics ASAP 2000 instrument. The sample was dried prior to the measurement at 200 °C for 24 h. Next, the sample was cooled down to 77 K and nitrogen isotherms were collected from P/P₀ = 10^{−6} to P/P₀ = 1.

2.3. Phenol alkylation with olefins

2.3.1. Reaction procedure

Catalytic reactions were performed in a stainless steel 600 mL batch reactor equipped with a sample port, stirring, and heating control system. Stirring was kept constant at 1000 rpm and the reaction pressure was autogenous. Reactants were introduced in the sequence olefin/catalyst/phenol at ambient temperature after which the heating profile was started. Reaction time was considered after reaching the reaction temperature. The default reaction time was 2 h and samples were taken from the closed reactor at the beginning and at the end of the reaction. Samples were stored in 10 mL amber flasks, which were kept in a freezer at −10 °C for further analysis. For samples from the heterogeneous reactions, the reaction mixture was filtered to remove the A-15 catalyst, while the samples from homogeneous reactions were passed through a column with sodium sulfate for neutralization.

In the first phase of the study, reactions with H₂SO₄ and A-15 were conducted under the same reaction conditions, in order to compare catalyst performance. These conditions were equal for both olefins and are summarized in Table 1. Catalyst concentrations are expressed relative to the phenol mass.

In the second phase of this study, the effects of different reaction conditions were evaluated for both reactions using A-15 as the catalyst. Factorial experimental design was carried out, by

Table 1

Reaction conditions used for comparing the H₂SO₄ and A-15 catalyzed phenol alkylation reaction with olefins.

Variable	Value
Temperature (°C)	150
Phenol mass (g)	94.11
Phenol/olefin molar ratio	1:1
Catalyst concentration (% w/w) ^a	1

^a In relation to phenol mass.

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