

# Catalytic Technique of Bio-oil Conversion to Valuable Chemicals

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**Abstract:** Catalytic technique of lignin derived bio-oil conversion, has been studied over Pt- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in a fixed-bed tubular micro-activity flow reactor at 673 K, 14 bar and space velocity 3 (g of Anisole)/(g of catalyst × h), in the presence of H<sub>2</sub>. A reaction network according to selectivity-conversion data is proposed to describe the evolution of products observed. The reactions include the following, anisole to benzene via HDO, to hexamethylbenzene via hydrodeoxygenation and alkylation, to phenol via hydrogenolysis, to 2-methylphenol via transalkylation and finally to 2, 4-dimethylphenol, 2, 4, 6-trimethylphenol and 2, 3, 5, 6-tetramethylphenol via transalkylation and alkylation. Experimental results indicated that the anisole conversion decreases about 20% with increasing the pressure from 8 to 14 bar at 673 K.

**Keywords:** Bio-oil, Valuable Chemicals, Anisole, Catalytic Conversion, Hydrodeoxygenation

## 1. Introduction

To begin to meet the needs for renewable fuels, many researchers have turned their attention recently to a massive resource that today finds few applications: lignin [1, 2]. Bio-oils derived from lignin are poor fuels, being unstable and having undesirable physical properties, and so they require upgrading. A potentially valuable processing goal is to convert lignin to bio-oils and to subject the bio-oils to hydrodeoxygenation (HDO), a chemical conversion that takes place at high H<sub>2</sub> partial pressures (as high as 100–200 bar) and high temperatures (250–400°C) to remove oxygen primarily in the form of water [2-7]. Oxygen-containing products, in addition to water, include CO<sub>2</sub>, formed in decarboxylation reactions, CO, and methanol. The upgrading classes of reactions include decarboxylation, hydrogenation, hydrogenolysis, hydrocracking, and dehydration [8-10]. Experimental investigations of anisole conversion with various catalysts have led to the inference that specific catalyst functions are responsible for specific reaction pathways. This work considers the potential use of lignin-derived bio oil as possible renewable fuel and chemical feedstock source.

Anisole is representative of bio-oils compounds that incorporate C<sub>methyl</sub>-O-C<sub>aromatic</sub> moieties—which are prevalent

in lignin as well as lignin-derived bio-oils. In the HDO of anisole, four reaction pathways—demethylation, hydrogenation, hydrogenolysis, and methyl group transfer (transalkylation)—occur, not all of them leading to the removal of oxygen. Because the C<sub>methyl</sub>-O bond is weaker than the C<sub>aromatic</sub>-O bond, demethylation via the rupture of the C<sub>methyl</sub>-O bond is typically favored kinetically [11-13].

The catalytic species that accelerate the HDO reactions include metals, metal sulfides, metal phosphides, metal carbides, and metal nitrides. These have been used on various supports, and in general the acidic supports catalyze methyl group transfers and also lead to catalyst deactivation by carbonaceous deposits (coke) that form on their surfaces.

Experimental investigations with various catalysts have led to the inference that specific catalyst functions are responsible for specific reaction pathways. Runnebaum *et al.* [14] reported that a noble metal (platinum) catalyzes phenol formation, and phenol is subsequently converted to benzene by breaking of the C<sub>aromatic</sub>-O bond and then to cyclohexane by hydrogenation of the aromatic ring, which is followed by hydrogenolysis of the C<sub>alicyclic</sub>-O bond. Transalkylation was found to be kinetically significant when the catalyst contained an acidic function, such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

serving as the support [14].

Ardiyanti *et al.* [8] investigated the catalytic hydroprocessing of anisole with monometallic and bimetallic catalysts (Ni–Cu supported on  $\delta$ - $\text{Al}_2\text{O}_3$ ) and observed that the bimetallic catalyst had a higher activity than a monometallic nickel catalyst. Li *et al.* [11] considered the conversion of anisole catalyzed by  $\text{Ni}_2\text{P}/\text{SiO}_2$  and  $\text{MoP}/\text{SiO}_2$ , as well as  $\text{NiMoP}/\text{SiO}_2$  with various Ni/Mo ratios, and they found that the nickel phosphide-containing catalysts, especially  $\text{Ni}_2\text{P}/\text{SiO}_2$ , are more active than conventional  $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$ . They concluded that the activity and stability of the phosphide catalyst increases with increasing Ni/Mo ratios.

Yang *et al.* [13] considered the influence of supports of nickel-containing catalysts on selectivity in anisole HDO, finding that reducible oxide supports such as  $\text{TiO}_2$  and  $\text{CeO}_2$  give high selectivities to aromatic products; they found an increasing trend for formation of benzene over cyclohexane in the series Ni/C, Ni/Al–SBA–15, and Ni/ $\gamma$ - $\text{Al}_2\text{O}_3$ . They attributed this trend to carbon deposits on nickel sites that reduced the hydrogenation activity, favoring aromatic formation instead. In related work, Huuska [15] investigated the effects of catalyst composition on the hydrogenolysis of anisole on molybdenum and nickel catalysts. They observed that when the catalysts were supported on an acidic oxide the main products were phenol and methyl-substituted phenols—because methyl group transfer is catalyzed by acidic sites. In contrast, when the support was not acidic, only limited methyl group transfer occurred, and the main products were phenol and cyclic hydrocarbons. In an investigation of anisole HDO catalyzed by mesoporous silica (SBA–15 and SBA–16)-supported CoMoW catalysts, Loricera *et al.* [16] represented the benefits of the high support surface area and the opportunities to vary the framework compositions.

The literature of catalytic HDO has been reviewed recently [2]; it includes numerous reports characterizing the conversion of whole bio-oil feedstocks, but there is a lack of fundamental understanding of the reactions. In present study, the catalytic upgrading of anisole to valuable chemicals in the presence of  $\text{H}_2$  over platinum supported on alumina ( $\text{Pt}/\text{Al}_2\text{O}_3$ ) is studied, regarding anisole as an excellent compound to represent lignin-derived bio-oils.

## 2. Experiment

Catalytic reaction experiments were carried out with a fixed-bed tubular micro flow reactor. The  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst pellets ( $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$  pellets containing 1 wt% Pt, Sigma-Aldrich) were placed on the porous plate in the reactor, mixed with about 2 g of inert  $\alpha\text{-Al}_2\text{O}_3$  beads. The catalyst in a mixture of  $\text{N}_2$  and  $\text{H}_2$  (50–50 volume percent) flowing at 20 l/h of was heated to the desired reaction temperature and held at this temperature for 20 min prior to the start of liquid reactant flow (anisole 99.8%, purchased from Merck). Fresh catalyst (0.25–2 g) was used for each

experiment, and each experiment was typically run for 6 h of continuous operation.

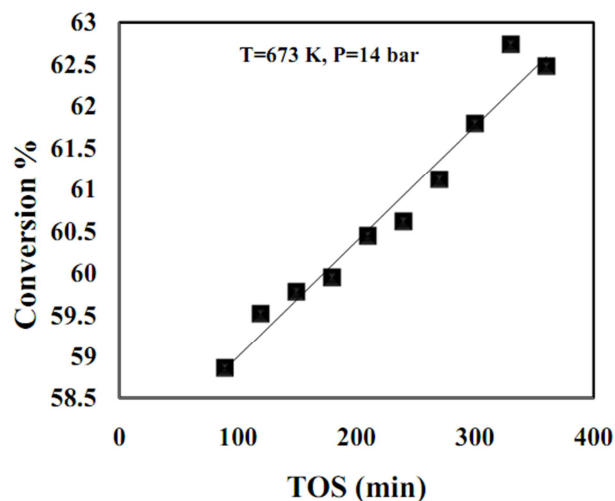
The catalytic conversion of anisole was carried out at 673 K and 14 bar; the liquid anisole flow rate was 0.03 mL/min, and the  $\text{N}_2$  and  $\text{H}_2$  flow rates were each 20 l/h. The value of the weight hourly space velocity (WHSV) was either 3 (g of anisole)/(g of catalyst  $\times$  h), varied by changing the catalyst mass and liquid flow rate. Anisole conversion ( $X$ ) and selectivity to various products  $i$  ( $S_i$ ) was defined as:

$$X = \frac{(\text{moles of Anisole})_{\text{in}} - (\text{moles of Anisole})_{\text{out}}}{(\text{moles of Anisole})_{\text{in}}} \times 100\% \quad (1)$$

$$S_i = \frac{\text{molar flow rate of product } i}{\text{molar flow rate of Anisole consumed}} \quad (2)$$

## 3. Results and Discussion

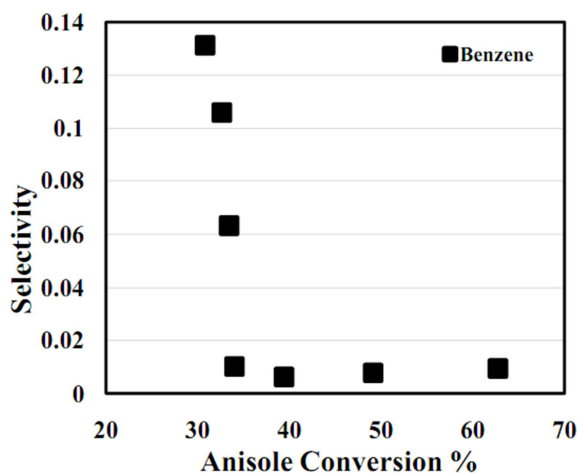
The major products of anisole upgrading identified by GC–MS were found to be benzene, phenol, 2-methylphenol, 2, 6-dimethylphenol, 2, 4, 6-trimethylphenol, 2, 3, 5, 6-tetramethylphenol, and hexamethylbenzene. Trace products that were identified only qualitatively were toluene, *o*-xylene, *p*-xylene, 4-methylphenol, 2, 3-dimethylphenol, 2, 4-dimethylphenol, 2, 6-dimethylanisole, 2, 3, 5-trimethylphenol, 3, 4, 5-trimethylphenol, 2, 3, 4, 6-tetramethylphenol, cyclohexane, methylcyclohexanone, and methylcyclohexane. The conversion of anisole catalyzed by  $\text{Pt}/\text{Al}_2\text{O}_3$  as a function of time on stream (TOS) is shown in Figure 1.



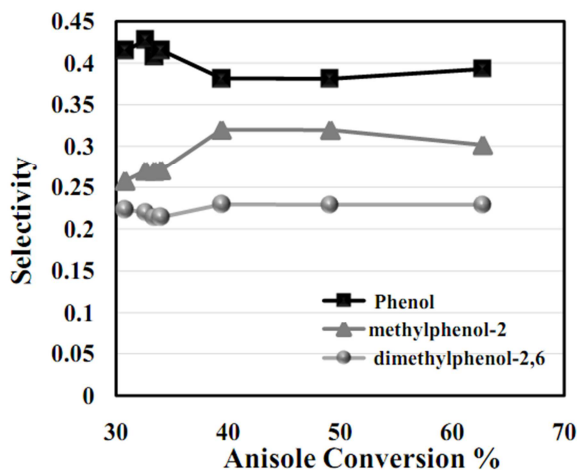
**Figure 1.** The conversion of anisole catalyzed by  $\text{Pt}/\text{Al}_2\text{O}_3$  as a function of time on stream (TOS) at  $\text{WHSV}=3$  g anisole/ (g catalyst $\times$ h).

Figures 2–4 represents the selectivity for the formation of the main products in the conversion of anisole to valuable chemicals catalyzed by  $\text{Pt}/\text{Al}_2\text{O}_3$  in the presence of  $\text{H}_2$  at 673K. From this figure it can be observed that selectivity to alkylation and transalkylation is more than HDO reaction [15, 26, 27]. The selectivity–conversion data for anisole indicate that benzene, phenol and 2-methylphenol are primary products and that 2, 6-dimethylphenol, 2, 4, 6-

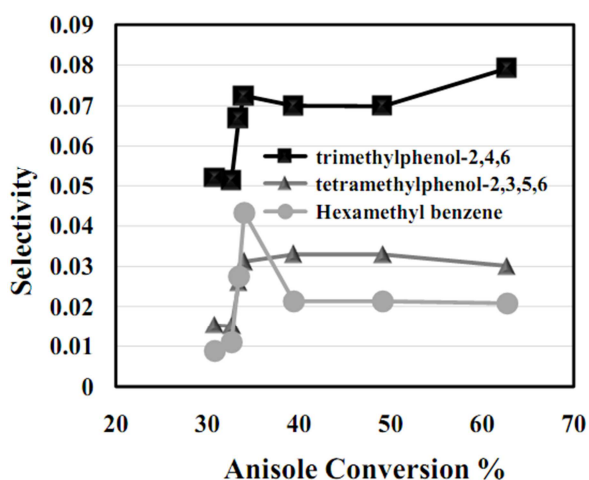
trimethylphenol, 2, 3, 5, 6-tetramethylphenol and hexamethylbenzene are higher-order products.



**Figure 2.** Selectivity for the formation of benzene in the conversion of anisole catalyzed by Pt/Al<sub>2</sub>O<sub>3</sub> in the conversion of anisole in the presence of H<sub>2</sub> at 673 K.

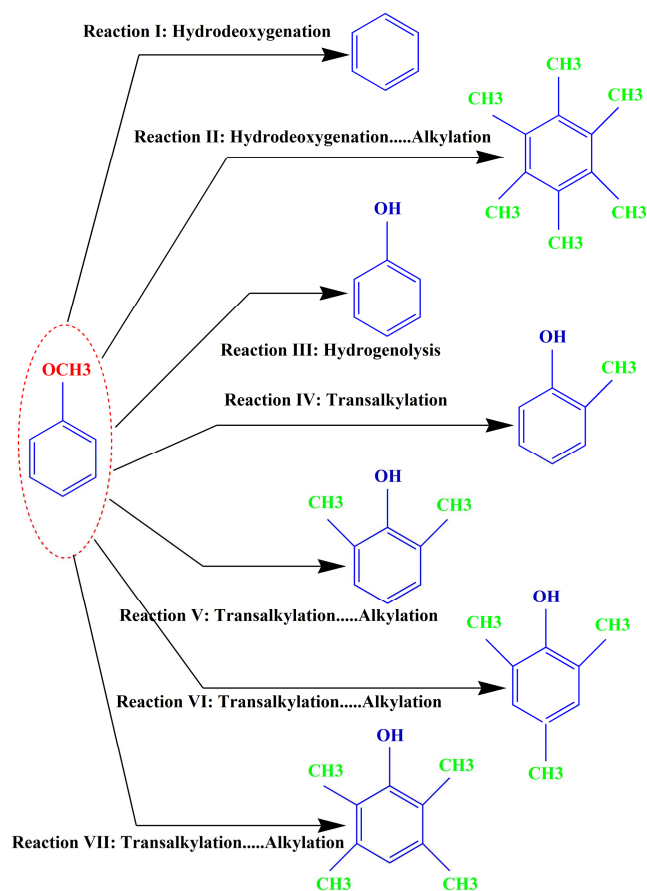


**Figure 3.** Selectivity for the formation of phenol, 2-methylphenol and 2, 6-dimethylphenol in the conversion of anisole catalyzed by Pt/Al<sub>2</sub>O<sub>3</sub> in the presence of H<sub>2</sub> at 673 K.



**Figure 4.** Selectivity for the formation of 2, 4, 6-trimethylphenol, 2, 3, 5, 6-tetramethylphenol and hexamethylphenol in the conversion of anisole catalyzed by Pt/Al<sub>2</sub>O<sub>3</sub> in the presence of H<sub>2</sub> at 673 K.

Reaction network development is based on determination of the likely reaction classes by identification of the main products in the conversion of anisole catalyzed by Pt/Al<sub>2</sub>O<sub>3</sub>. The main products investigation indicates that the important kinetically reaction classes are as follow: formation of phenol by Hydrodeoxygenation reaction; formation of benzene by hydrodeoxygenation reaction; formation of 2-methylphenol by Transalkylation reaction; formation of 2, 6-dimethylphenol, 2, 4, 6-trimethylphenol, 2, 3, 5, 6-tetramethyl phenol and hexamethylbenzene by Alkylation reaction. The reactions giving the most abundant products in the conversion of anisole catalyzed by Pt/Al<sub>2</sub>O<sub>3</sub> at 673 K and 14 bar are represented in Figure 5. The products and reactions are consistent with those observed previously [15].



**Figure 5.** The main reactions to most abundant products based on analysis of selectivity-conversion plots for the conversion of anisole and H<sub>2</sub> catalyzed by Pt/Al<sub>2</sub>O<sub>3</sub> at 5673 K.

Figure 6 represents the variation of anisole conversion as a function of WHSV at different operating temperature. It is obvious that anisole conversion decreases with increasing WHSV.

The effect of pressure on anisole upgrading process is considered in Figure 7. Based on reported data in Figure 7, the anisole conversion at 673 K and WHSV=3 (g of anisole)/(g of catalyst × h) decreases from 50% to 30% with increasing the pressure from 8 to 14 bar, but enhancing the pressure more than 14 bar has not significant effect on conversion. It seems that increasing the pressure not only has

not positive effect on anisole conversion, it decreases the rate of reactions.

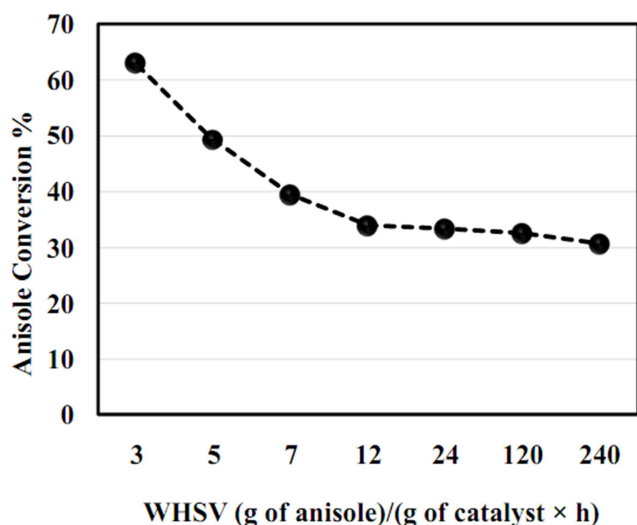


Figure 6. The conversion of anisole catalyzed by Pt/Al<sub>2</sub>O<sub>3</sub> as a function of WHSV at  $p=14$  bar and  $T=673$  K.

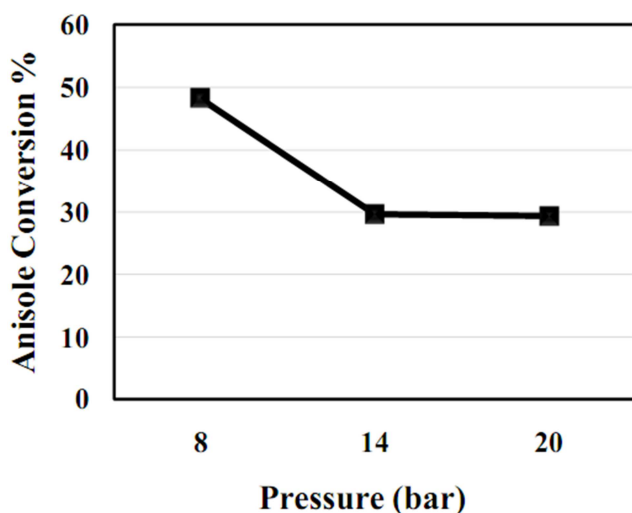


Figure 7. The conversion of anisole as a function of pressure at 673 K and WHSV=3 g anisole/ (g catalyst×h).

As a model reaction development, the upgrading process of anisole has been considered, and the reaction network represented in Figure 8. The main reaction routes during the upgrading process of anisole are hydrogenation, hydrogenolysis, hydrodeoxygenation, transalkylation and alkylation. In the present study, benzene, phenol, hexamethylbenzene, 2-methylphenol, 2, 6-dimethylphenol, 2, 4, 6-trimethylphenol and 2, 3, 5, 6-tetramethyl phenol were detected as the main products, whereas no methyl anisole, cyclohexanol and cyclohexanone were observed. Hydrogenolysis or demethylation takes place on the metal surface to form phenol. Another reaction involves direct deoxygenation, leading to methanol and benzene. Also using catalysts that incorporate both metal and acid functions such as Pt/Al<sub>2</sub>O<sub>3</sub>, in addition to direct deoxygenation, transalkylation and HDO are catalyzed by acidic sites. So the

combination of a noble metal and an acidic support provide a higher catalytic activity.

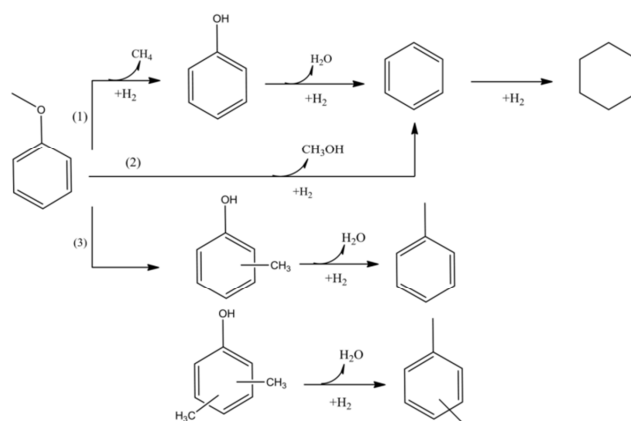


Figure 8. Reaction network for the conversion of anisole catalyzed by Pt/Al<sub>2</sub>O<sub>3</sub> at 673 K and 14 bar.

## 4. Conclusions

In this work a reaction network for catalytic upgrading of anisole on the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst is developed. The experimental data indicated that the platinum catalyzed hydrogenolysis of the anisole to produce phenol as the significant primary product under the applied operating conditions (673 K and 14 bar). Other main products were produced by alkylation, transalkylation and HDO reactions. The main products that were detected in relatively high yields include benzene, formed by HDO of anisole or phenol, hexamethylbenzene formed by alkylation of benzene, 2-methylphenol formed by transalkylation of anisole and alkylation of phenol, and finally 2, 6-dimethylphenol, 2, 4, 6-trimethylphenol and 2, 3, 5, 6-tetramethylphenol formed by subsequent alkylation of 2-methylphenol.

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