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Simultaneous upgrading of furanics and phenolics via hydroxyalkylation/aldol condensation reactions

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Abstract:

The simultaneous conversion of cyclopentanone and m-cresol has been investigated on a series of solid acid catalysts. Both compounds are representative of biomass-derived streams. Cyclopentanone can be readily obtained from sugar-derived furfurals via Piancatelli rearrangement under reducing conditions. Cresol represents the family of phenolics, typically obtained from the depolymerization of lignin. In the first biomass conversion strategy proposed here, furfural is converted in high yields and selectivity to cyclopentanone (CPO) over metal catalysts such as Pd-Fe/SiO_2 catalyst at 600 psia H_2 and 150°C. Subsequently, CPO and cresol are further converted via acid-catalyzed hydroxyalkylation. This C-C coupling reaction may be used to generate products in the molecular weight range that is appropriate for transportation fuels. Since molecules beyond this range may be undesirable for fuel production, a catalyst with suitable porous structure may be advantageous for controlling the product distribution in the desirable range. In fact, when Amberlyst resins were used as a catalyst, C_{12}-C_{24} products were obtained, whereas when zeolites with smaller pore sizes were used, they selectively produced C_{10} products. Alternatively, CPO can undergo the acid-catalyzed self-aldol condensation to form C_{10} bicyclic adducts. As an illustration of the potential of practical implementation of this strategy for biofuel production, the long chain oxygenates obtained from hydroxyalkylation/aldol condensation were successfully upgraded via hydrodeoxygenation to a mixture of linear alkanes and saturated cyclic hydrocarbons, which in practice would be direct drop-in components for transportation fuels. Aqueous acidic environments, typically encountered during the liquid-phase upgrading of bio-oils would inhibit the efficiency of base-catalyzed process. Therefore, the proposed acid-catalyzed upgrading strategy is advantageous in terms of process simplicity for biomass conversion.

Introduction

Fossil sources exhibit undoubted technological and economical advantages for production of chemicals and transportation fuels. However, emission of greenhouse gases (CO_2 and CH_4) is an issue of critical concern regarding global warming and climate change. This concern has led to increased research efforts with the goal of commercializing fuels and chemicals from biomass sources that would greatly reduce the carbon footprint. However, techno-economic evaluations indicate that immediate implementation is not possible. The great variety of oxygenated compounds with incompatible chemistries makes a single-stage upgrading practically impossible. Therefore, greater efforts are needed to help in the development of more efficient biomass upgrading technologies with a number of unit operations that make the process economically feasible. Although several strategies have been investigated to process vapors and liquids derived from biomass pyrolysis, finding efficient processes that can be techno-economically attractive has been challenging [1]. The direct catalytic hydrotreating of condensed bio-oil faces major problems [2, 3], including low yields of liquids in the fuel range and high hydrogen pressures, which complicates their integration with a pyrolysis system [4]. Incorporation of pre-hydrogenated bio-oils into conventional petroleum feedstocks in refinery operations, such as the fluidized catalytic cracking (FCC) and hydrotreating units [5, 6] have also shown technical

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impediments that may obstruct their implementation in commercial processes. Some important advances have been made in the upgrading of pyrolysis vapors that leads to enhanced stability of the condensed liquid by forming C-C bonds before adjusting the oxygen content [7, 8].

In the last few years, we have investigated possible conversion paths for separated vapors and liquids obtained from fractionation of bio-oil via step-wise condensation of pyrolysis vapors [9, 10] as well as multistage pyrolysis process [11, 12]. The core of this approach is to carry out the sequence of thermal treatments by heating the biomass at increasing temperatures so that the bio-oil is fractionated into different streams, each one enriched in either light oxygenates, or sugar-derived compounds, or phenolics-derived compounds, respectively [11, 12]. Accordingly, by segregating each specific group of functional molecules in a separate fraction, a combined catalytic upgrading strategy can be developed more selectively and effectively, exploiting the different chemistries of each fraction and optimizing the upgrading instead of a single hydrotreating step for the full bio-oil [13-15].

The fraction of light-oxygenates is rich in acetic acid, acetol, and acetaldehyde. We have previously proposed [14] that they could undergo ketonization to produce acetone, which in turn could be coupled with furfural, an abundant component in the sugar-derived stream, to produce C_8-C_{13} oxygenates over basic catalysts [16, 17]. Alternatively, instead of directly condensing with acetone, furfural can also be pre-stabilized into key intermediates to diminish carbon losses and humins formation, a major cause of catalyst deactivation. The intermediate products are still functional, so they can be further upgraded (C-C bond-chain enlarged) to a wide range of desirable products.

Hydrogenation-decarbonylation of furfural to furan compounds (i.e., methyl furan, dimethyl furan) [18, 19], ring rearrangement of furfural to cyclopentanone (CPO) via Piancatelli reaction [20-22], or oxidation of furfural to carboxylic acids [23, 24] are outstanding examples of furfural conversion into more stable forms that have been recently reported in the literature. In the so-called Sylvan process, methyl furan is condensed with different types of carbonyl compounds, such as acetone, butanal, or furfural [25, 26] to elongate the carbon chain and bring the products to the fuel range. Dimethyl furan can also be coupled with ethylene via Diels-Alder reaction to produce valuable aromatics such as p-xylene [27]. Specific strategies for upgrading biomass-derived furanics via C-C coupling reaction have been analyzed in our recent review [28].

Interestingly, Hronec et al. [29, 30] have shown that the Piancatelli ring rearrangement in reducing condition is also a promising route to stabilize furfural into cyclopentanone. This is a remarkable pathway, because the O heteroatom is removed from the ring, producing CPO a useful chemical and potential building block for C-C coupling reactions [29]. Although the Piancatelli ring rearrangement of furfuryl alcohol readily occurs in hot liquid water without the need of an additional catalyst, hydrogenation is required to first hydrogenate the CO group in furfural, as well as the resulting C=C double bond after the ring closure to obtain CPO. For this reaction, noble metal catalysts such as Pt, Pd, Ru, Ir as well as inexpensive metals such as Ni, Cu have been used in the conversion of furfural in aqueous phase under H_2 pressure [31, 32]. For example, over 75% yield of CPO has been reported over Pt/C or Ni-CNTs [22, 33]. High selectivity toward cyclopentanone is a definite techno-economic advantage of this approach compared to other upgrading strategies. For the Piancatelli rearrangement, the presence of liquid water plays a crucial role in the reaction [20, 22, 30]. Moreover, the presence of acetic acid in the reaction mixture provides a positive effect on the yield of the desired products [29]. That is, components that are naturally present in biomass-derived streams, i.e., aqueous solutions with high acidity, favor the occurrence of this reaction. Not only CPO is a very convenient building block for carbon retention in the liquid fuel range, but reaching high conversions of furanics to this single molecule greatly reduces catalyst deactivation by avoiding the typical resinification of furfurals to humins. From all of this, we propose that the path of furanics to cyclopentanone is a very effective strategy for upgrading of furfural-rich streams [28].

The phenolics fraction can also be used to effectively incorporate into the fuel range those oxygenates that are too small to be directly hydrotreated. That is, converting C_2-C_4 oxygenates to alcohols greatly facilitates their incorporation via alkylation. For example, iso-propanol, obtained from hydrogenation of acetone, can produce hydrocarbons in a molecular weight range suitable for the gasoline/diesel pool. Corma et al. [25, 34, 35] have pointed out the feasibility of forming C-C bonds between carbonyl compounds with other organic molecules whenever their electron-density is high enough to promote the electrophilic-attack of the oxonium ion

generated by the protonation of the carbonyl group. Phenolics compounds such as m-cresol and guaiacol, abundant species in biomass pyrolysis vapors, are suitable candidates as hydroxyalkylation aromatic substrates. In fact, several studies have reported successful examples of hydroxyalkylation in systems comprising acetaldehyde/p-cresol [36], acetaldehyde /phenol [37], formaldehyde/guaiacol [38], acetaldehyde/o-xylene [39], aldehyde/benzene derivatives [40, 41], acetone / phenol [42], benzaldehyde/benzene derivatives [43], paraformaldehyde /anisole [44], formaldehyde/benzene [45], formaldehyde / phenol [46] over acid-functionalized solids, such as Amberlyst acidic resin and acidic zeolites to produce crucial platforms for the chemical industry. For example, Rode et al. [47] have reported 80-95% yields of coupling products from the reaction of acetaldehyde/p-cresol over Hβ and bentonite clay catalysts impregnated with dodecatungstophosphoric acid.

In this contribution, we propose a novel approach for the simultaneous upgrading of furfural and m-cresol, two model compounds that represent two streams of sequential biomass thermal treatment at moderate and high temperatures. In this strategy, furfural is first pre-stabilized as cyclopentanone via the Piancatelli rearrangement/hydrogenation process [22, 48]. This intermediate product is then used to hydroxyalkylate m-cresol and generate C_{10}-C_{24} oxygenates, a suitable range for transportation fuel precursors.

Results and Discussion

1. Hydroxyalkylation of m-cresol/cyclopentanone

a) *Product distribution over solid acid Amberlyst 15:*

The hydroxyalkylation of m-cresol and CPO yields various cyclopentyl-substituted cresol compounds including (3), (4), (5) and (6) (HAA products) as shown in path B **Scheme 1**. Two products from self-aldol condensation of cyclopentanone including (1) and (2) (AC products) were also observed, as shown in path A. In most cases, the formation of product (2) is negligible compared to that of the other products; therefore, in most runs, product (1) is the only representative of the self-aldol condensation reaction.

Figure 1 shows the reaction data obtained after 2 h in a batch reactor on Amberlyst 15 in the temperature range 65-145ºC at a 2:1 m-cresol/CPO molar feed ratio. The results demonstrate that the acid resin displays an acceptable activity, with conversion increasing from 8 to 38% as the temperature increases, keeping a good carbon balance. For instance, 13% CPO conversion was obtained at 100ºC, with 40% selectivity to AC products, 60% selectivity to HAA products and a carbon balance of 98%. Higher temperatures favor the formation of monomer and dimer coupling products (1, 3, 4, and 5). Above 120ºC, the decomposition of the trimer (6) becomes evident and undesired reactions start to occur. For example, at 145ºC, the carbon balance dropped from almost 100 to 83 %, most probably due to polymerization as indicated by the change in color of the solution. One problem associated with the use of a resin catalyst like Amberlyst 15 is the decomposition of the polymeric matrix that may become significant as temperature increases.

The acid-catalyzed formation of AC products is in itself an interesting outcome of the study since the aldol condensation of cyclopentanone has been typically reported over basic catalysts, such as MgO, KF/Al_2O_3, $CaO\text{-}CeO_2$, CaO, magnesium–aluminum hydrotalcites (MgAl-HT) and lithium–aluminum hydrotalcites (LiAl-HT) [48], or even in NaOH solutions [30]. While it is widely known that the aldol condensation can be catalyzed by both bases and acids, the latter has seldom been reported for cyclopentanone. Zou *et al.* [49] reported the self-aldol condensation of cyclopentanone and cyclohexanone in glass reactor over MOF-encapsulating phosphotungstic, Amberlyst 15 and HZSM-5 materials. The reaction was conducted at 130ºC in pure cyclic ketone for 48h and moderate conversion of the ketones could be obtained. However, no information related to carbon balance was reported.

In this work, the experiments were conducted in a Parr reactor in more controlled and quantitative ways than previous studies with shorter reaction times and direct measurement of the carbon balance. The results summarized in **Figure 2** confirm that solid acids such as Amberlyst 15 are capable of producing acceptable yields of AC products (1+2). The yield of the monomer (1) increases over time, reaching 16% after 6 hrs of reaction. The amount of dimer product (2) is very small, reaching only about 1% yield. Excellent carbon balances of 94-97% were observed in both cases. Although the reaction conditions and catalyst formulations will need to be optimized to enhance the yield to coupling compounds, these preliminary results are promising enough to be considered an interesting approach for biomass conversion, particularly since the acidic environment is

commonly found in bio-oil upgrading. The high content of water in real pyrolysis mixtures would require to operate in biphasic system [50]. Implementation of the concepts derived from model compound studies in the separation and conversion of bio-oil to fuel may demonstrate the advantage of using solid emulsifier materials such as hydrophobized zeolites [51, 52] nanotubes, and other amphiphilic catalysts that stabilize emulsions [53] to achieve maximized adducts yields for the reaction.

b) Comparison of different solid acid catalysts:

Based on these observations, several solid catalysts with different characteristics, including a resin with higher acid density (Amberlyst 36), a microporous zeolite (Hβ), and a mesoporous acid catalyst (SiO_2-Al_2O_3) were investigated and compared to a homogeneous catalyst, para-toluene sulfuric acid (p-TSA) to explore the effect of catalyst topology and acidity. To make a proper comparison of selectivity, we adjusted the reaction temperature to reach an overall CPO conversion of about 15 %. Specifically, the activity comparison was made at 100ºC for Amberlyst and p-TSA, and at 250ºC for Hβ, SiO_2-Al_2O_3. The results are summarized in **Table 1** and **Figure 3.** Amberlyst 36 shows an analogous behavior to Amberlyst 15, reaching 15% CPO conversion with selectivities of 38% and 62% for AC and HAA products, respectively. Interestingly, while (at 100°C) Amberlyst resins catalyzed the generation of both AC and HAA, the zeolite Hβ and amorphous SiO_2-Al_2O_3 yielded only AC products (at 250°C).

It is possible that the drop in HAA selectivity might be due to different steric constrains in the catalysts. For instance, Amberlyst resins have large cavities that may allow the formation and desorption of the relatively large HAA products (see example of products 3, 4, 5 and 6 in **Scheme 1**). By contrast, the more constrained Zeolite Hβ may only allow the smaller AC products (93% selectivity) leave the zeolite, while the HAA, if formed will remain trapped inside the microporous structure. It is suggestive that the homogenous p-TSA exhibits a higher selectivity to large HAA products (3 + 4 + 5 + 6) (**Figure 3**) in comparison to the behavior of solid catalysts. More specifically, at comparable CPO conversion (15-20%) the yields of 3, 4, 5 and 6 were 2.4%, 1.7%, 0.16% and 0.4% on Amberlyst 36 while they are much higher, reaching 5.2%, 1.3%, 1.8% and 12.4%, respectively with the homogeneous catalyst p-TSA.

To check the effect of reaction temperature to the product distribution, reaction runs were conducted on zeolite Hβ at different temperatures (100-250°C). As shown in the **Table 1**, the selectivity on this zeolite did vary with temperature. Higher selectivity toward HAA is favorable as the temperature deceases. This observation agrees with those obtained from homogeneous catalysts in which low temperature favors the formation of HAA products rather than AC products.

Table 1. Activity and Average pore size of sceened catalysts

Catalyst	T, ºC	Conversion, %	Selectivity, %		Yield, %		Acid density, mmol/g_{cat}	Conversion per site (mol.L^{-1}.$mmol_{acid}^{-1}$)	Carbon balance, %	Average pore size, nm
			AC	HAA	AC	HAA				
p-TSAa	100	20	9.3	90.7	2.9	27.5	5.8[c]	1.3	97	-
Amberlyst 15[a]	100	12.8	39.6	60.4	3	3.5	4.7[c]	0.6	94	29[c]
Amberlyst 36[a]	100	15.3	38	62	4.5	4.6	4.9[c]	0.7	94	24[c]
Zeolite Hβ[b]	100	6.8	-	-	-	-	0.75[d]	2.02	90	0.6[f]
	120	11	71.1	28.9	0.2	0.045		3.38	93	
	200	11.7	85	15	2.9	0.2		3.48	92	
	250	16.3	93	7	11	0.5		4.86	94	
SiO_2-Al_2O_3[b]	100	0.76	-	-	-	-	0.53[e]	0.32	98	4.8[g]
	150	1.14	-	-	-	-		0.48	99	
	200	5.42	99	1	0.9	0.004		2.29	95	
	250	17	98	2	10.4	0.1		7.26	96	
	280	33.8	95	5	21.6	0.7		14.3	85	

[a]Glass reactor; [b]Parr reactor; [c]reported by manufacturer; [d]measured by TPD-isopropyl amine [e]ref [54] [f]ref. [55], [g]measured by BET-N_2 ads./des.

However, at this point, it can be concluded that although the temperature can change product distribution, the porous characteristic of solid acid catalysts is the dominant factor that makes AC products dominant (i.e., over 70% sel. at 120ºC). At 100ºC, no adducts were observed. In the case of SiO_2-Al_2O_3, the same analysis was conducted with temperature range from 100 to 280ºC. Interestingly, high selectivity towards AC is observed in all cases. With a large pore size, (average 4.8 nm) and rather slow reactions, one would not expect internal mass transfer limitations on this mesoporous material. As shown in **Figure 4a**, the variation of overall CPO conversion as a function of temperature indicates an apparent activation energy of about 50 kJ/mol, while on the Hβ zeolite, which is clearly affected by mass transfer limitations, the apparent activation energy is only 4.5kJ/mol. Moreover, when the product yields are used for the Arrhenius plot (**Figure 4b**), apparent activation energy values of about 90 and 140 kJ/mol are obtained for AC and HAA formation, respectively.

The low activity exhibited by the amorphous silica-alumina catalyst towards formation of HAA products could be due to the relatively weak acid strength of this material. Indeed, calorimetry measurements of ammonia adsorption on SiO_2-Al_2O_3 give evidence of much lower density of strong acid sites than Amberlyst or any zeolite [56, 57]. Therefore, the acid strength of the mesoporous silica-alumina might not be high enough for catalyzing HAA reaction. That is, only materials with strong acidity and large pore structure could be effective catalysts for the HAA reaction.

To gain a deeper understanding of the pathway for HAA product formation on zeolite Hβ, several separate runs were conducted at 250°C with varying amounts of catalyst. As seen in **Figure 5a, b** the yields of HAA and AC products uniformly increase with the amount of catalyst, as expected. At the same time, it is observed that while the selectivity to product (3) dominates at low yields (at the lowest catalyst mass) the selectivity to products (4) and (5) increased with overall conversion which demonstrates the expected series/parallel sequence for this reaction, i.e., CPO → (3); followed by (3) → (4) or (3) → (5). In this case, no traces of product (6) were observed

Another series of independent runs was conducted, keeping the catalyst mass constant while varying temperatures. As shown in **Figure 5c**, contrary to the behavior of Amberlyst 15 and 36, which were able to achieve measureable yields (7-9%) at low temperatures (100-120ºC), the Hβ catalyst only generated small amounts of condensation products at these temperatures (traces of AC and HAA products were detected). It is conceivable that the diffusion of these large products out of the micro-porous structure is greatly hindered at low temperatures in this zeolite, leading to some disappearance of CPO, but without the formation of any noticeable coupling products. **Figure 5d** shows the distribution of HAA products from zeolite Hβ as a function of reaction temperature. At low temperatures (100-120ºC), the major product is (5), which is necessarily produced from product (3). By contrast, at higher temperatures, the selectivity towards product (5) decreases while that to (3) increases. Clearly, at high enough temperatures, product (5) begins to decompose via C-C cleavage yielding back product (3). The low selectivity towards product (4) might be due to the higher abundance of m-cresol with respect to CPO (m-cresol/CP feed ratio = 2:1).

In fact, as shown in **Table 1**, the carbon balance is over 90% for all cases. That is, by using a less reactive intermediate such as cyclopentanone, not only the carbon losses can be minimized, but valuable condensation products can be obtained with less humins formation.

c) Effect of temperature on the competition between self-aldol condensation (AC) and hydroxyalkylation (HAA):

The investigated reaction, in fact, is complicated since two possible parallel reactions are taking place at the same time. The relative rate between two pathways depends on factors such as feed ratio, temperature, etc. Moreover, the porous characteristic of each solid catalyst places different influence in the diffusion of formed products and so on the obtained product distribution. A series of experiments was conducted with a homogeneous catalyst (para-toluene sulfuric acid) to get an insight into the nature of this reaction. In this case, there is no possible role of porous cavities affecting the product distribution as in solid acid catalysts. As shown in **Figure 6a**, at low temperatures (e.g., 60ºC), hydroxyalkylation products (HAA) dominate, with selectivity above 90%. As temperature increases, the selectivity toward aldol condensation products (AC) slowly increases (up to 150ºC) but beyond this temperature, it jumps dramatically from 20% at 200ºC to 60% at 250ºC. The change of product distribution with increasing temperature in this case might be due to the low stability of the HAA C-C coupling

products (the alcohol) that makes it easily decomposed back to CPO and m-cresol at high temperature (250ºC) before dehydration. This results in more abundant AC products at 250ºC.

At the lowest temperature, only the C-C coupling monomer (3) is observed in the products. However, at 100ºC, the trimer (6) is formed easily, becoming one of the most abundant products and reaching 45% selectivity. As the temperature is further increased, the selectivity to (6) greatly decreases with the other products increasing, even when the reactant conversion remained unchanged. It is clear that (6) starts decomposing back to monomer (3). Indeed, negligible amounts of the trimer (6) are detected at 250ºC. Likewise, as shown previously (**Figure 1**), similar decomposition of the trimer (6) is observed over the solid acid Amberlyst 15 at temperatures above 120ºC. **Figure 6b** also shows similar trends for the trimers (4) and (5), which initially increase with temperature, but then decrease, reaching a maximum selectivity at 200ºC (~20%).

The possible reaction mechanism includes four primary steps: (a) protonation of cyclopentanone on acid sites to form an enolate, (b) C-C coupling of the activated CPO with another CPO or m-cresol to form condensation products (ACol and HAAol), (c) deprotonation, and (d) dehydration of the resulting alcohols to generate the AC and HAA products. It is possible that the rate limiting step for each reaction could be one of those. However, in the presence of acid catalysts the dehydration step is relatively fast. It should be noted that the relative activation energy between each step could be shifted, depending on catalysts with different acid strength. More detailed kinetic and theoretical studies are required on each individual reaction to obtain a more comprehensive understanding of the system.

d) Effect of feed ratio:

Both AC and HAA can yield products with longer carbon chains, which can subsequently be hydrodeoxygenated to molecules that directly fall in the gasoline/diesel range. In some applications, in may be desirable to produce a narrow molecular weight distribution. In this case, our results show that a narrower molecular weight distribution can indeed be obtained by adjusting the m-cresol/CPO feed ratio. As illustrated in **Figure 7**, as the m-cresol/CPO increases from 2:1 to 5:1, the yield of AC products drops from 4.5% to 1.4% while that of HAA products increases from 3.7 to 5.4%. Interestingly, when the m-cresol/CPO ratio increases to 7:1, only HAA products are obtained with no traces of AC products.

2. Hydrodeoxygenation of coupling products obtained in the first step

Hydrodeoxygenation is the final step after accomplishing the desired molecular weight via C-C coupling. For practical implementation as fuels, the coupling compounds generated from hydroxyalkylation would need to be saturated and deoxygenated to produce alkanes with properties similar to those derived from petroleum energy sources. To demonstrate the sequence, first, the C-C coupling step was carried via HAA reaction on a 3g Amberlyst 36 sample in a Parr reactor (150ºC, m-cresol/CPO=2:1, 12h). In this step, the goal is to obtain a reasonable yield of coupling products, which can be used later as feedstock for the HDO upgrading. In this case, 51% CPO conversion with a wide range of long-chain oxygenates was obtained, as shown in **Figure 8**, with (1) and (3) as major products, accounting for 18% and 14% yield, respectively.

To carry out the HDO upgrading step, 2 ml of the liquid product of the previous step was diluted in 118 ml of undecane solvent together with 500 mg of 2% Pd/Al_2O_3 catalysts. The catalyst was reduced at 150ºC for 3 h under 400 psia of H_2. The HDO run was conducted at 250ºC in the batch reactor for 12 h. The most abundant products were cyclopentane and methyl cyclohexane, which come from the hydrogenation/dehydration of CPO and m-cresol. Long-chain hydrocarbon products include fully saturated C_{10} alkanes, C_{12} cyclic and C_{12} alkane products which are generated from the ring opening of the saturated species (1) and hydrogenation of (3), followed by the ring opening, respectively (**Scheme 2** and **Figure 9**). Trace amount of carbon chain longer than 12 was observed, which is probably due to the decomposition of dimer/trimer at the high temperatures and long reaction time used in this experiment. The observed alkanes represent over 39% selectivity of the upgraded liquid. In fact, hydrogenated products derived from m-cresol, such as methylcyclohexane or methylcyclohexanol, also fall into gasoline range (C_7-C_{12}). Therefore, the whole applicable products in the fuel range would account for 90% of the upgraded liquid. More interestingly, the carbon balance for the HAA and HDO steps are 96% and 95%, respectively, resulting in over 90% efficiency for the whole catalytic upgrading process, which starts from CPO and results in with drop-in liquid fuel

products. This promising result illustrates the great potential of this strategy for biomass-derived liquid fuel production.

Conclusions

The Piancatelli rearrangement of furanic compounds to CPO represents a very attractive biomass upgrading strategy that pre-stabilizes reactive molecules such as furfural into a useful and less reactive ketone. Compared to conventional hydrogenation/hydrogenolysis strategies, this approach demands less energy and less H_2 consumption. In addition, the high water and acid content of bio-oil are in fact favorable for this conversion, which makes the process more appealing in terms of practical implementation. The production of this stable intermediate can be followed by C-C bond formation reactions, such as self-aldol condensation or hydroxyalkylation with phenolics-derived fractions. When the C-C bond forming process is followed by a hydrodeoxygenation step a mixture of C_{10}-C_{16} hydrocarbons, which are in the gasoline/diesel range can be effectively obtained. For example, when the product stream from the AC/HAA reaction of CPO and m-cresol was followed by HDO on a bifunctional catalyst over 90% efficiency of the whole catalytic upgrading process starting from CPO was demonstrated, which highlights the potential of this strategy for future biofuel applications.

The major obstacle of this approach is that the large organic molecules produced by the HAA reaction are trapped in microporous catalysts, particularly at low temperatures. Thermally stable zeolites that can be operated at higher temperatures show a lower degree of trapping, but the problem still subsists. Further research on acidic materials with hierarchical structures with a proper mesoporous/microporous balance that minimizes the diffusion path of large adducts out of the catalyst cavities would be desirable.

Experimental Section

The conversion of furfural to cyclopentanone was carried out in a Parr reactor at 150ºC, 14-40 bar for 6 hrs in water solvent over 0.15 g 2% Pd-Fe/SiO_2 catalyst, at an initial concentration of furfural of 200 mM. The hydroxyalkylation of m-cresol with cyclopentanone was conducted at atmospheric pressure in a glass reactor in the temperature range 65-140ºC, for 2 hrs in the presence of Amberlyst 15, Amberlyst 36, or p-TSA (Sigma Aldrich) catalysts. Alternatively, the reaction was conducted in a Parr reactor at 100-250ºC, under 300 psia N_2 for 2 hrs in the presence of Zeolite Hβ (Zeolyst) or SiO_2-Al_2O_3 (Sigma Aldrich). In all cases, the amount of catalyst used was 0.15 g and the feed was either pure CPO or m-cresol/CPO mixtures. The effect of m-cresol/CPO ratio (2:1, 5:1, and 7:1) on the product distribution was examined in the Parr reactor at 120ºC, 300 psia N_2 for 2 hrs in the presence of 1 g Amberlyst 15 in decalin solvent. The aldol condensation of cyclopentanone was examined in Parr reactor at 100ºC and 300 psia N_2 for 2 and 6 hrs. 0.5M of CPO in decalin solvent over 1 g Amberlyst 15.

The product mixture was analyzed by Shimadzu QP2010S gas chromatograph/mass spectrometer (GC-MS) and quantified by GC-FID Agilent 6890 equipped with a flame ionization detector for quantification. Both GC's were equipped with a Zebron ZB-1701 column with dimensions of 60m x 0.25 mm x 0.25 µm.

The conversion (X), yield and selectivity were calculated as:

$$X = \frac{C_{CPO-in} - C_{CPO-out}}{C_{CPO-in}} \quad ; \quad Y_i = \frac{C_i \times n}{C_{CPO-in}} \quad ; \quad S_i = \frac{C_i}{\sum C_i}$$

The carbon balance for the HAA reaction was calculated as:

$$Carbon\ \ balance = \frac{C_{CPO \rightarrow products} + C_{CPO-out}}{C_{CPO-in}}$$

The carbon balance for the HDO step was calculated as:

$$Carbon\ \ balance = \frac{\sum C_i \times n_{Ci}\big|_{product}}{\sum C_i \times n_{Ci}\big|_{feed}}$$

where C_{CPO}(in, out): Concentration of cyclopentanone before and after reaction;

C_i: Concentration of each product;

n: Number of cyclopentanone molecule in molecular structure of products;

nC_i: Number of carbons in molecular structure

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Keywords: C-C coupling 1 • hydroxyalkylation 2 •phenolics 3 • cyclopentanone 4 • biofuels 5

Layout 1:

FULL PAPER

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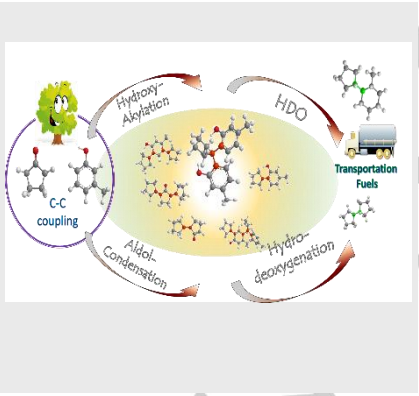
We are here proposing an attractive strategy to effectively upgrade two fractions of torrefraction simultaneously via hydroxyalkylation/ adol condensation reactions. As the results, after HDO processing, saturated alkanes with carbon chain ranging from C_{10}-C_{16} could be obtained, which could be used as transportation fuel or refinery feed.



*Tuong V. Bui, Dr. Tawan Snooknoi, Prof. Daniel E. Resasco**

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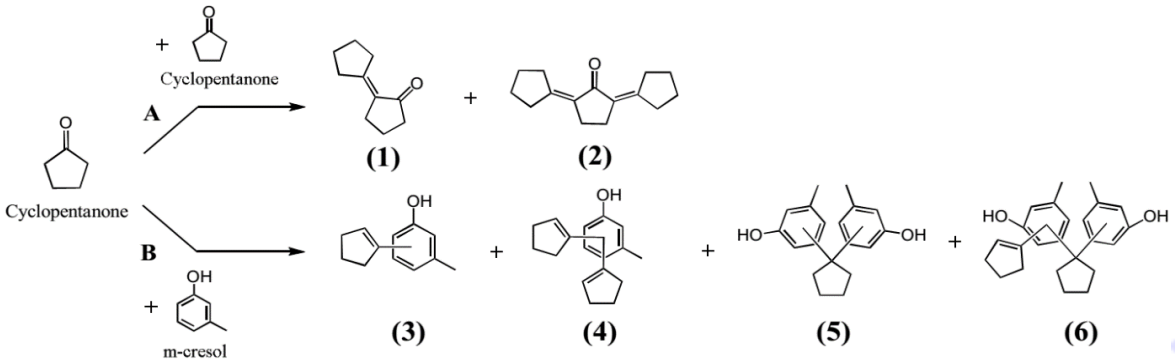
Figures and Schemes



Scheme 1. Products from hydroxyalkylation of m-cresol and cyclopentanone

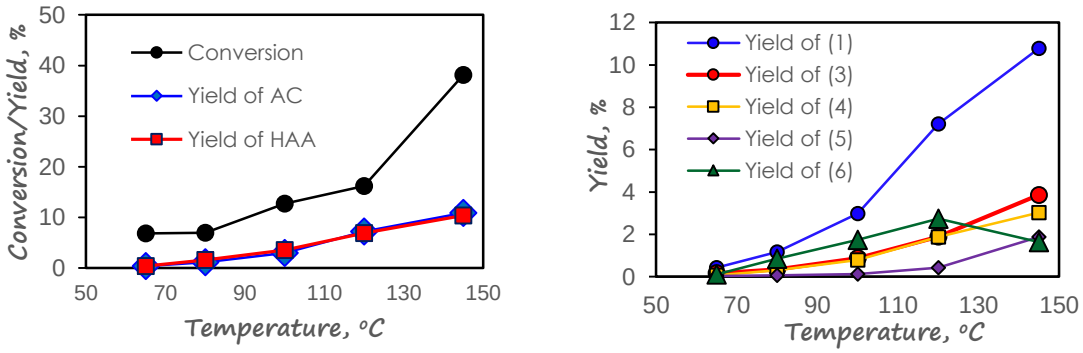


Figure 1. Catalytic performance of Amberlyst 15 at different temperatures. Product (1) – (6) are presented in Scheme 1

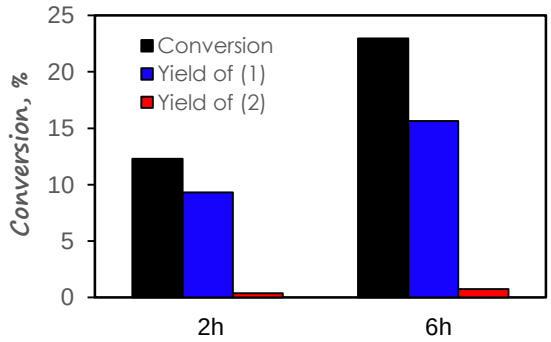


Figure 2. The acid-catalyzed aldol condensation of cyclopentanone over Amberlyst 15 (Parr reactor at 100°C and 300 psia N_2 for 2 and 6 hrs in decalin solvent over 1 g Amberlyst 15.)

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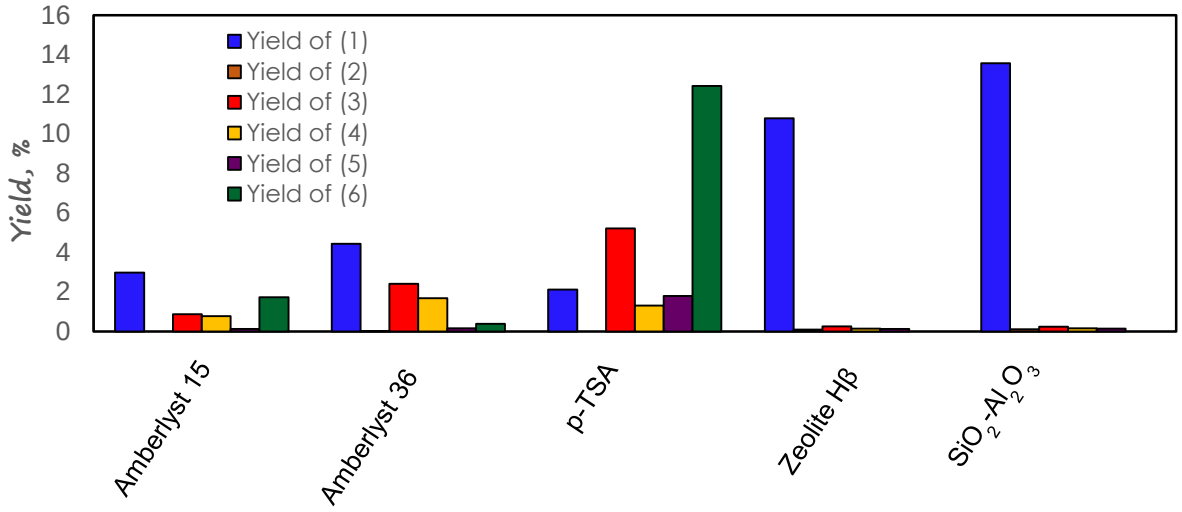


Figure 3. Yield of coupling products from different catalysts at comparable CPO conversion

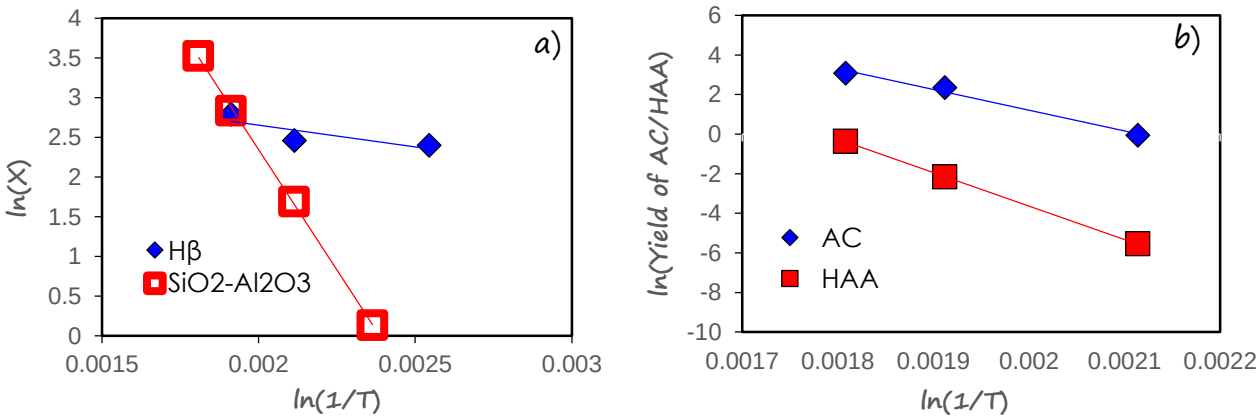
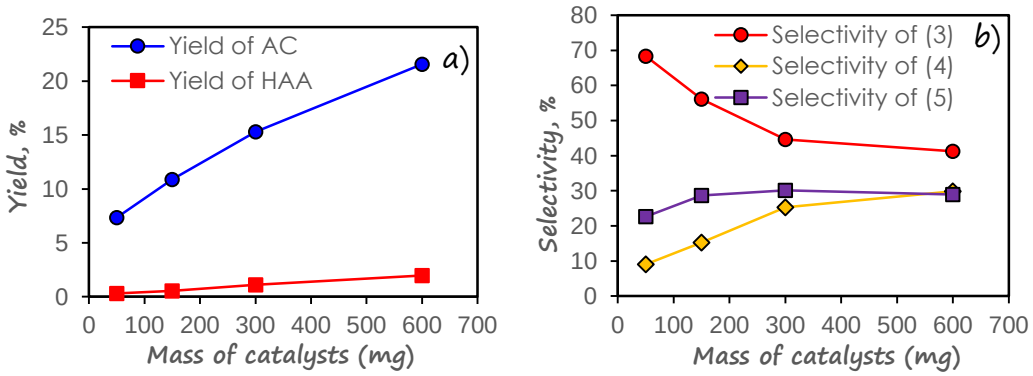


Figure 4. Arrhenius plots for a) overall CPO conversion over Hβ and SiO_2-Al_2O_3; and b) Yield of AC and HAA products over SiO_2-Al_2O_3.



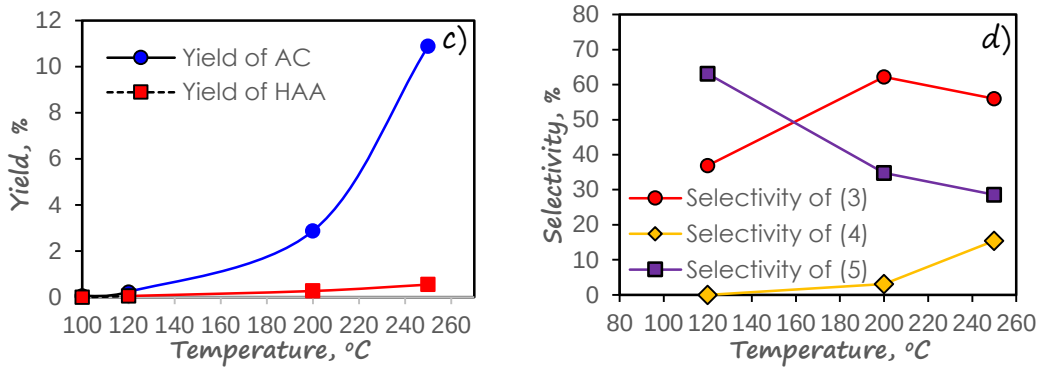


Figure 5. a) Yield of AC, HAA products and b) Distribution of HAA products at different mass of catalysts c) Yield of AC and HAA products and d) Distribution of HAA products at different temperatures

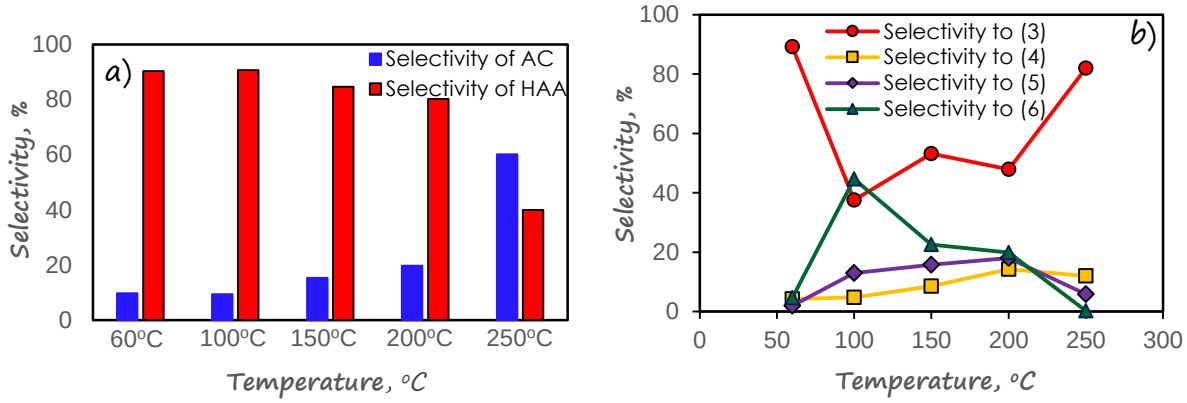


Figure 6. a) Selectivity of aldol condensation and hydroxylalklyation products (AC and HAA) at different temperatures (Reaction condition: m-cresol/cyclopentanone=2/1, Parr reaction, reaction volume 120ml, the conversions at 60°C, 100°C, 150°C, 200°C, 250°C are 20%, 20%, 23%, 21%, 20%, respectively) b) Selectivity of hydroxyalkylation products at different temperatures

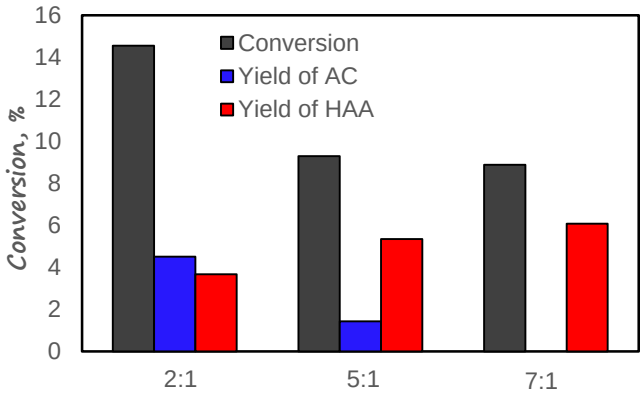


Figure 7. The distribution of AC and HAA products at different m-cresol/CPO ratios over Amberlyst 15 (Parr reactor at 120°C, 300 psia N_2 for 2 hrs in the presence of 1 g Amberlyst 15 in decalin solvent)

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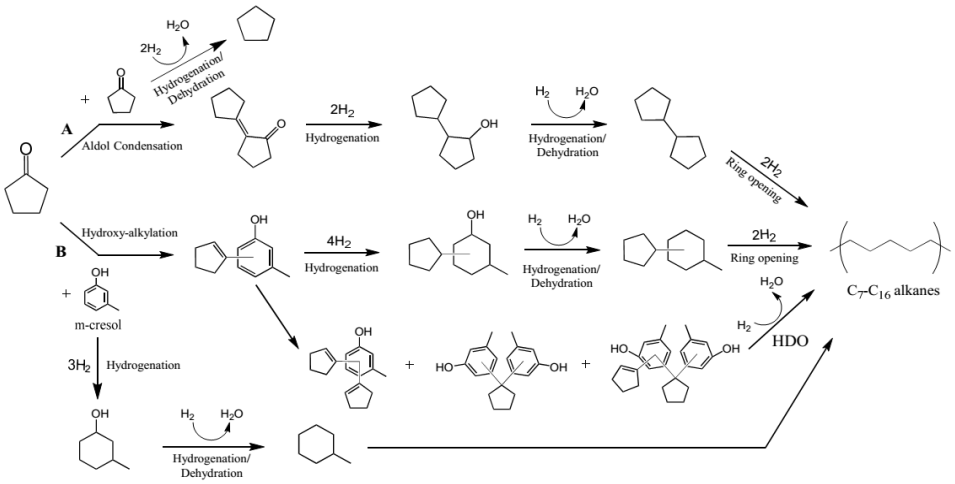

Scheme 2. Biofuel production scheme starting from cyclopentanone

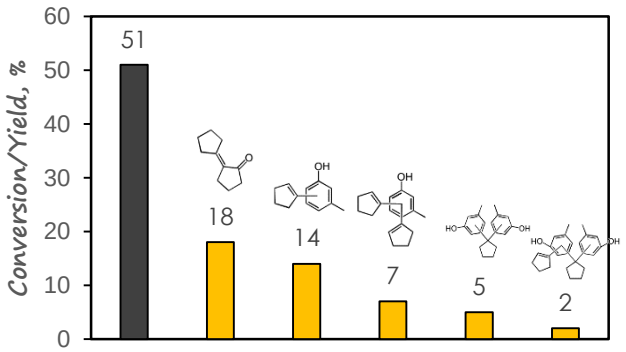

Figure 8. *Conversion/Yield of HAA reaction between CPO and m-cresol (dash-black bar is the conversion of CPO, yellow bars are the yield of each product)*

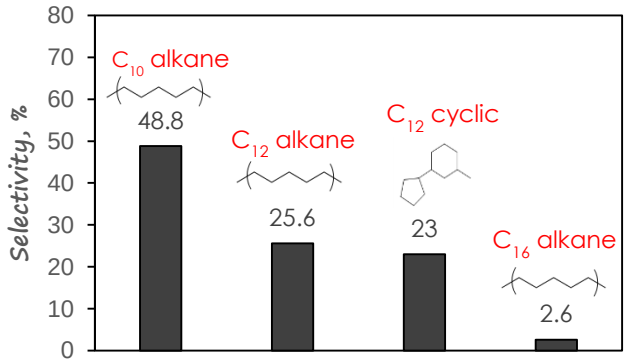

Figure 9. *Selectivity of each saturated products in HDO upgraded liquid*

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Graphical abstract