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Development of 6-amyl- $\alpha$ -pyrone as a potential biomass-derived platform moleculeMd. Imteyaz Alam<sup>a,†</sup>, Shelaka Gupta<sup>a,†</sup>, Ashish Bohre<sup>b</sup>, Ejaz Ahmad<sup>a</sup>, Tuhin S. Khan<sup>a</sup>, Basudeb Saha<sup>b,c,\*</sup>, M. Ali Haider<sup>a,\*</sup>Received 00th January 20xx,  
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**Catalytic transformation routes for the valorization of biomass-derived 6-amyl- $\alpha$ -pyrone (6PP) were explored for the first time. Ring-opening and decarboxylation of 6PP in water yielded non-2-en-4-one with 95% conversion and nearly 60% selectivity at 498 K, without the requirement of an acid catalyst. The decarboxylated product was further hydrogenated to yield 4-nonanone over a Pd/C catalyst. In order to produce longer chain hydrocarbons of diesel and jet fuel ranged compounds, C-C coupling via aldol condensation of nonanone with furfural and 5-hydroxymethyl furfural (HMF) was experimented over a mixed oxide (CaO-MgO) catalyst measuring upto 40% and 60% yield of the branched aldol products at 443 K and 393 K respectively.**

In an effort to produce fuels and chemicals from biomass, considerable attention is given to the development of novel processes, producing long-chain and branched hydrocarbons. One prominent strategy, proposed by Dumesic and co-workers,<sup>1,2</sup> involves the synthesis of ketones from biomass-derived platform molecules (i.e. biomass-based building block molecules utilised to produce a variety of chemicals and fuels)<sup>3-8</sup>. In this method, catalytic upgrading of biomass was carried out to produce C<sub>9</sub> linear ketones having direct application as a fuel additive or upgrading to gasoline and diesel.<sup>2</sup> The reported method, essentially requires the integration of several steps, which include; the conversion of lignocellulosic biomass into C<sub>6</sub> sugars, dehydration of sugars to HMF, rehydration and ring-opening of HMF to levulinic acid (LA), hydrogenation and cyclization of LA to  $\gamma$ -valerolactone (GVL), ring-opening and hydrogenation of GVL to pentanoic acid and subsequent ketonization via a C-C coupling reaction to produce 5-nonanone.<sup>2,9</sup> Understandably, for commercial success, the method needs to be simpler that involves fewer steps and utilizes

inexpensive catalysts. Thus, in this study, a novel strategy is proposed to produce unsaturated/saturated C<sub>9</sub> linear ketones directly from biomass in two or three steps. The proposed method is based on the ring-opening and decarboxylation of 6PP yielding unsaturated C<sub>9</sub> linear ketones. 6PP is obtained directly from solid-state fermentation of the lignocellulosic biomass.<sup>10</sup> At present, 6PP is used in food industry as a coconut aroma ingredient<sup>11</sup> for enhancing flavour of soft drinks, yogurts etc. Species of *Trichoderma* are known to produce 6PP on solid-state fermentation of waste biomass such as sugar cane bagasse or industrial agricultural waste.<sup>10</sup> Since 6PP is toxic to the fungal growth, extractive fermentation techniques have been applied to increase the yield up to 7.1 g/l.<sup>12</sup> Interestingly, 6PP can also serve as a potential platform chemical to yield fuel-ranged hydrocarbons via further processing. We have performed ring-opening and decarboxylation of 6PP in aqueous phase to achieve high yield of non-2-en-4-one without the requirement of an acid catalyst. The reactivity of 6PP towards ring-opening and decarboxylation resembled to the structurally analogous triacetic acid lactone (TAL), a biomass-derived platform molecule.<sup>13</sup> 6PP, having unsaturation in the lactone ring, underwent this reaction at a relatively mild condition compared to the saturated lactones (e.g. GVL), wherein; high temperature (>573 K) and an acid catalyst is required.<sup>14</sup>

Experimental results showing the representative reactions of 6PP undergoing ring-opening and decarboxylation in water-THF solvent, with and without an acid catalyst are presented in Table 1. Complete conversion (up to 95%) of 6PP was obtained at 498 K in water-THF mixture in 8 hours, without the requirement of an acid catalyst (Table 1, Entry 1). The selectivity towards the product (non-2-en-4-one) was measured to be 58%. Reaction in water was not tested due to the immiscible nature of 6PP. On performing this reaction in THF as the solvent and in presence of silica-alumina catalyst, 6PP conversion was reduced to 18% (Table 1, Entry 2), which was due to the residual water present in THF. Therefore, water was considered to be absolute essential to carry out this reaction, which appears as the reactant in reaction stoichiometry as shown in Scheme 1.

<sup>a</sup> Renewable Energy and Chemicals Laboratory, Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz Khas, Delhi 110016, India

<sup>b</sup> Laboratory of Catalysis, Department of Chemistry, University of Delhi, Delhi 110007, India

<sup>c</sup> Catalysis Center for Energy Innovation, University of Delaware, Newark, DE 19713, USA

Tel: +91-11-26591016, Fax: +91-11-2658-2037

E-mail: [imteyaz84@gmail.com](mailto:imteyaz84@gmail.com), [bsaha@udel.edu](mailto:bsaha@udel.edu), [haider@iitd.ac.in](mailto:haider@iitd.ac.in)

\* Corresponding Authors

† Equal first author contribution

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**Scheme 1.** Ring opening and decarboxylation of 6PP into non-2-en-4-one

Compared to TAL, 6PP requires a relatively higher temperature for ring-opening and decarboxylation, the reasons for which could be attributed to the absence of a  $\beta$ -keto group which facilitates ring-opening and decarboxylation in TAL.<sup>15</sup> Interestingly, earlier work on TAL had considered the hydroxyl (or ketone functionality) substitution at the  $\beta$ -position to be essential for ring-opening and decarboxylation of the 2-pyrone-ring.<sup>15,16</sup> Remarkably, 6PP without having any hydroxyl substitution, showed relatively easier ring-opening and decarboxylation at a lower temperature as compared to the saturated lactone. On reducing the reaction temperature to 463 K, the conversion and product selectivity was reduced to 55% and 41% respectively (Table 1, entry 3). 6PP conversion in water was fitted to the Arrhenius equation (Figure S5) and the apparent activation energy was calculated to be 166 kJ/mol. As suggested for TAL, the rate-determining step is likely to be ring-opening.<sup>15</sup> Figure 1a shows the elementary steps required for ring-opening of 6PP in water. The ring-opening reaction proceeds in two steps, nucleophilic addition of water on the carbonyl-carbon (C2) which leads to the ring-opening via a proton transfer to the ring-oxygen (O1). DFT calculations estimated the intrinsic activation barrier for the water addition step to be 180 kJ/mol (Figure 1a), which is comparable to the experimentally measured value.

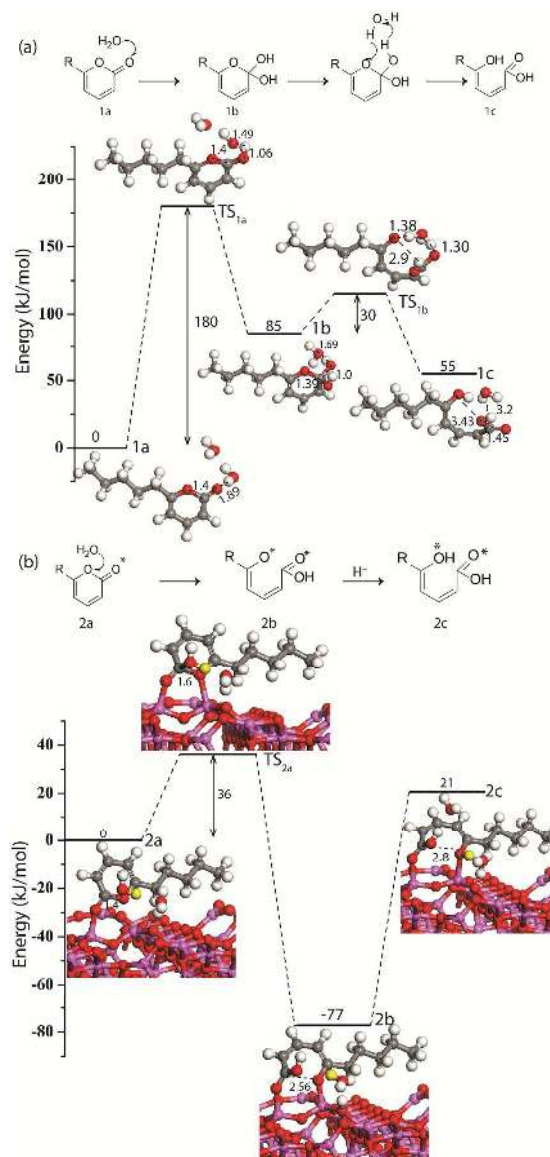
**Table 1.** Reactivity results for the ring-opening and decarboxylation of 6PP into non-2-en-4-one

Entry	Substrate	T (K)	t (h)	Catalyst	% C	% S
1	6PP	498	8	-	95	58
2	6PP*	498	8	Silica-alumina	18	78
3	6PP	463	8	-	55	41
4	6PP	473	10	Silica-alumina	>99	65
5	6PP	463	8	Silica-alumina	77	65
6	6PP	463	8	$\gamma$ -Alumina	75	65

Substrate = 2 wt% of solvent; total volume of the solvent = 50 ml; solvent THF:water = 3:1; catalyst = 50 wt % of substrate; T, temperature; t, time; C, Conversion; S, Selectivity, \*THF alone solvent medium

In presence of an acid catalyst, the ring-opening and decarboxylation is likely to be accelerated. The Brønsted acidic protons facilitate proton transfer to the ring (O1) or carbonyl oxygen (O2), leading to the formation of stable carbenium or oxocarbenium ions in water for subsequent ring-opening.<sup>17</sup> In contrast, Lewis acidic systems are expected to provide a greater control on product selectivity with reduced conversion as observed in case of GVL ring-opening and decarboxylation.<sup>18</sup> Indeed, on performing the reaction in water-THF solvent mixture on a silica-alumina catalyst, an appreciable increase in conversion (>99%, Table 1, Entry 4) was measured at 473 K compared to the non-catalytic aqueous system (Table 1, Entry 1). The acid catalyzed conversion remained higher (~77%) even at a reduced temperature of 463 K compared to the non-catalytic system (Table 1, entry 3). Interestingly, the reaction on the Lewis acidic  $\gamma$ -alumina catalyst showed similar results. The conversion and product selectivity values (Table 1, entry 6) measured at 463 K for  $\gamma$ -alumina are

comparable to the values measured for silica-alumina (Table 1, entry 5). The Arrhenius fits for both the catalysts estimated an apparent activation energy of 99 kJ/mol for  $\gamma$ -alumina and 125 kJ/mol for silica-alumina (Figure S5). The results, however; stand in contrast to the reported reactivity trend for GVL ring-opening and decarboxylation; wherein varying total yields measuring 89% and 59% of the decarboxylated product were observed over the silica-alumina and  $\gamma$ -alumina catalysts, respectively<sup>18</sup>.

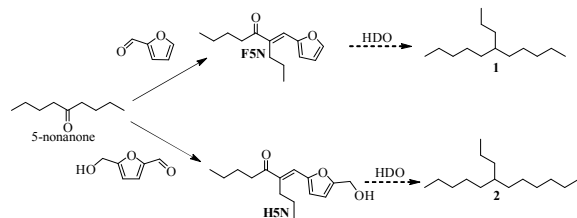


**Figure 1.** Reaction diagram for the ring-opening of 6PP in (a) non-catalytic aqueous system and (b) acid catalyzed system of  $\gamma$ -alumina.\*indicates the atom by which species is making a bonding interaction with the surface.

The ring-opening and decarboxylation of 6PP was accelerated with lower activation barriers in acid catalysts as compared to the non-catalytic system. An insight into the mechanism of the acid catalyzed reaction may be obtained from the DFT calculations for ring-opening of 6PP performed on the  $\gamma$ -alumina surface. The {110}

surface of  $\gamma$ -alumina was chosen for studying the ring-opening reaction.<sup>19</sup> The 6PP molecule is preferentially adsorbed at the tri-coordinated aluminum center, Al(III) on the  $\gamma$ -alumina (110) surface by forming a bond between the carbonyl oxygen (O2) and surface Al(III) atoms. The ring-opening of 6PP proceeds with a nucleophilic water addition to the carbonyl carbon (C2) leading to acyl cleavage and hydrogen transfer (from the water) to the surface oxygen. In the ring-opened structure (Figure 1b, 2b) the molecule was adsorbed on the surface with both carbonyl-oxygen (O2) and ring-oxygen (O1) forming a bond with two neighboring surface Al(III) atoms. The intrinsic activation energy for the ring-opening step was calculated to be 36 kJ/mol (Figure 1b, 2a to TS<sub>2a</sub>). In the next step, the ring-oxygen was observed to receive back the proton from the surface oxygen to yield the same ring-opened intermediate (Figure 1b, 2c) as in non-catalytic aqueous system (Figure 1a, 1c). The proton-transfer step is endothermic and the activation energy for this step is likely to be higher than 98 kJ/mol (Figure 1, 2b to 2c). The apparent activation energy measured for the  $\gamma$ -alumina catalyzed reaction was 99 kJ/mol, which is comparable to the DFT calculated value. Unsaturated keto product obtained was hydrogenated to give 4-nonanone. On a Pd/C catalyst, hydrogenation was performed to give >99% conversion with 83% product selectivity at 373 K.

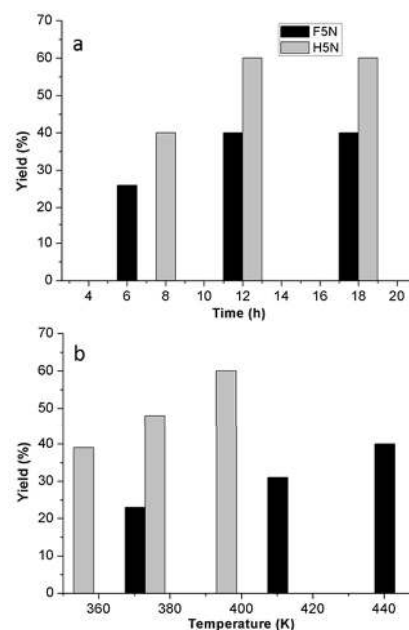
In order to introduce a valorization route for high volume market opportunity of 6PP, nonanone may be reacted with furanics (furfural and HMF) for C-C coupling to yield C<sub>14</sub> or C<sub>15</sub> range products. C-C coupling of the biomass-derived furanic intermediates with suitable carbonyl compounds is generally performed via aldol condensation or hydroxyalkylation/alkylation pathways.<sup>20,21</sup> These pathways for C-C coupling have been reported in our previous publications and by other researchers as well.<sup>22,23</sup> For example, an organocatalyst, 1,8-diaza-bicycloundec-7-ene showed significant improvement in C-C coupling reactivity of furan aldehyde with ketone and hydroxyl ketone.<sup>24–26</sup> Study on aldol reactions of biomass-derived furanics have utilized acetone as the reactant, wherein two or more consecutive crossed aldol reactions are necessary to yield C<sub>12</sub> or larger fraction drop-in biofuels<sup>20</sup>. Handling of acetone is also a problem because of high volatility and low flash point. Comparatively, nonanone is easier to handle and directly yield C<sub>14</sub>/C<sub>15</sub> fractions on reacting with furanics in a single aldol reaction, showing considerable merits. In addition, as pointed out by Chen *et al.* the condensation products of nonanones are likely to yield branched alkanes on hydrodeoxygenation (HDO) with higher octane numbers.<sup>27</sup> Furthermore, the aldol reaction with nonanone is carried out in neat conditions without the requirement of an organic solvent and thus reducing the cost of the process as compared to the furanic-acetone reaction.<sup>27</sup> All of the aforementioned reasons make the proposed process an attractive route.



**Scheme 2.** Reaction scheme showing base catalyzed aldol condensation products of 5-nonanone with furfural (F5N) and HMF

(H5N). Routes for HDO to yield branched alkanes are shown by dashed lines.

To demonstrate the C-C coupling route, 5-nonanone was allowed to condense with furanic aldehydes in presence of a Brønsted base to obtain adducts **F5N** and **H5N** as shown in Scheme 2. Dumesic, Huber and co-workers have shown the activity of mixed oxide catalysts to achieve higher yield of the crossed aldol products on reacting furanics with acetone.<sup>28</sup> Inspired by their work, Chen *et al.* have recently experimented with the aldol reaction of 3-pentanone with furfural in solvent free conditions to produce branched alkanes.<sup>27</sup> The authors reported a maximum 60% yield of the aldol product of 3-pentanone with furfural on the CaO catalyst at 443 K. Interestingly, the catalytic activity of the CaO catalyst for the aldol reaction was measured to be higher than that of the mixed oxides of MgO-ZrO<sub>2</sub>, MgO-La<sub>2</sub>O<sub>3</sub> and hydrotalcite of Mg-Al.<sup>27</sup> Encouraged by this, aldol reaction of 5-nonanone with furfural was experimented with CaO catalyst, under the same reaction conditions.<sup>27</sup> However, compared to 3-pentanone, the aldol product yield was significantly reduced to only 30% at 443 K in 8 hour.<sup>27</sup>



**Figure 2.** Yields of aldol condensation products (F5N and H5N) of 5-nonanone reaction with furfural and HMF, measured over (a) time and (b) temperature.

In order to achieve higher aldol product yield, mixed oxides of Ca and Mg were synthesized as the base catalyst for the aldol reaction of 5-nonanone with furanics. The XRD pattern showing the peaks corresponding to pure cubic phase CaO and periclase MgO is given in Figure S6 (a). In the XRD spectra, traces of some CaCO<sub>3</sub> and Ca(OH)<sub>2</sub> were observed, suggesting rapid carbonation and hydration of the mixed oxide in air and at room temperature which was further confirmed with the FT-IR spectrum (Figure S6 (b)) of the synthesized CaO-MgO catalyst.

Figure 2a and 2b shows the obtained yields of aldol products (F5N and H5N) at different temperature and time of reaction over the CaO-MgO catalyst. F5N yield measuring up to 40

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% was observed for a reaction between furfural and 5-nonanone at 443 K for 12 h, which was followed by a plateau on extending the reaction time as shown in Figure 2a. In case of HMF condensation with 5-nonaone, 40% yield of H5N was obtained at 393 K for 8 h. A 20% improvement in yield was observed on continuing the reaction for 12 h with a total yield of 60%. The reaction pattern suggested a faster rate of formation of F5N and H5N in the beginning of the reaction, followed by a slow rate. No improvement in yields of the products was observed when the reaction was conducted for 18 hours (Figure 2a). Higher yield of the aldol product measured on reacting 5-nonanone with HMF (as compared to furfural), likely due to the mesomeric effect of the electron withdrawing hydroxymethyl group in HMF which increases the positive charge density at the carbonyl carbon (C2) and thus facilitate a favourable C-C coupling with the carbanion.

The activity of the CaO-MgO catalyst could be attributed to the synergistic effect between the active phase of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the binary system of the mixed oxide. Both CaO and MgO are known for strong basic sites.<sup>28</sup> High basic site density of the catalyst is likely to facilitate the formation of the enolate intermediate by the abstraction of the  $\alpha$ -proton, accelerating the C-C coupling.<sup>20</sup> The branched aldol products (F5N and H5N) were obtained in liquid state at the room temperature, which may directly undergo HDO reaction to form  $\text{C}_{14}$  and  $\text{C}_{15}$  branched alkanes. The HDO route shown in Scheme 2 have been experimented previously to give high yield of the alkane product<sup>23,27,29</sup>. Chen et al. have performed experiments on the HDO of aldol product of 3-pentanone and HMF using  $\text{M}/\text{SiO}_2$  ( $\text{M}=\text{Fe}, \text{Cu}, \text{Co}, \text{Ni}, \text{Pt}$ ) catalysts and measured up to 95% carbon yield of the branched alkane product, with negligible fragmentation<sup>27</sup>. Our earlier study on HDO of the aldol product of HMF with acetone had shown similar results, yielding 96% alkane with Pd/Zelite- $\beta$  catalyst.<sup>23</sup> The recyclability of the catalyst was studied for the reaction between HMF and 5-nonanone for 12 h at 393 K. The results (Figure S9) showed a slight decrease in the yield of H5N from 60% to 48% corresponding to the 1<sup>st</sup> and 4<sup>th</sup> cycle, possibly due to a slight loss in measured basicity of the recovered CaO-MgO catalyst (Table S1).

Ketones, in general, may show different aldol reactivity based upon the position of the keto functionality resulting into varying  $\alpha$ -H reactivity and steric effect<sup>27</sup>. In order to study the effect of the position of the carbonyl group, aldol reactions of HMF with 2-nonanone and 4-nonanone were performed at 393 K for 12 h using the CaO-MgO catalyst (Figure S7 and S8). As compared to 5-nonanone, the obtained aldol product yield of HMF with 4-nonanone (57%) was negligibly reduced. However, the aldol reaction of HMF with 2-nonanone showed a slight increase (67%) in the product yield likely due to the less sterically hindered methyl group.

## Conclusions and Outlook

6PP obtained from the fermentation of lignocellulosic biomass shows a considerable potential to be developed as a platform molecule. 6PP underwent ring-opening and decarboxylation in presence of water, without the requirement of a catalyst. As compared to the non-catalytic reaction, the acid catalyzed ring-opening reactions were accelerated with relatively lower activation barriers. Experimentally measured apparent activation energy for the ring-opening and decarboxylation reaction in water was comparable to the DFT calculated intrinsic barrier for ring-opening,

which indicated ring-opening to be rate limiting. Similarly, for the acid-catalyzed reaction in water and in presence of  $\gamma$ -alumina, the measured apparent activation energy was comparable to the DFT calculated intrinsic endothermicity of the proton transfer step, which was essential for obtaining the ring-opened intermediate. Interestingly, in contrast to the reactivity trend reported for saturated lactones such as GVL, 6PP as an unsaturated lactone showed a different trend in reactivity with negligible change in conversion and product selectivity on the Brønsted and Lewis acid catalysts. A valorization route for 6PP was envisaged by performing aldol condensation reaction of nonanones with furfural and HMF. The reaction was performed in neat conditions without the requirement of an organic solvent. A mixed oxide catalyst of Ca and Mg was utilized for obtaining higher yields of the aldol products. The liquid aldol products may directly undergo catalytic upgrading via HDO to yield branched  $\text{C}_{14}$  or  $\text{C}_{15}$  alkanes to be used as diesel and jet range fuels.

Compared to TAL, 6PP as a biomass-derived 2-pyrone shows significant merits for development into a platform molecule. TAL is obtained from the fermentation of glucose.<sup>30</sup> In contrast, 6PP is obtained directly from the fermentation of lignocellulosic biomass. So far, the reported maximum yield for TAL by applying metabolic engineering is 5.2 g/l, which is lower than the reported maximum yield of 6PP.<sup>31,32</sup> Interestingly, improvement in 6PP yield has not been tried with the same rigor using any genetic engineering technique. Once produced in high yield, the fermentation process may be integrated to the catalytic process proposed in this work, to produce biorenewable fuels. Similarly, other valorization routes for 6PP may be explored. Structurally, 6PP is a 6-membered unsaturated, heterocyclic compound with a cyclic ester functionality. Numerous possibilities arise on exploring the reactivity of 6PP to produce fuels and chemicals. George Kraus and co-workers have shown the potential for converting the 2-pyrone (TAL) into 2-pyridones, to be used as pharmaceutical building blocks.<sup>33</sup> Furthermore, selective partial and complete hydrogenation of 6PP followed by ring-opening and decarboxylation will lead to a myriad of interesting products to be used as fuels, chemicals, polymers and pharmaceuticals.

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