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Production of renewable lubricants via self-condensation of methyl ketones†

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Self-condensation of biomass-derived methyl ketones catalyzed by solid bases or acids produces corresponding cyclic trimers exclusively in excellent yields. Condensates containing 24–45 carbon atoms are shown to be suitable lubricant base-oils after the removal of residual unsaturation and oxygen. Properties of cycloalkanes produced from biomass are very similar to those of conventional lubricant base-oils. The process reported here offers an environmentally benign alternative to the current non-selective production of lubricant base-oils from α-olefins, and avoids the production of corrosive waste products.

The past decade has seen significant progress in the development of renewable alternatives to fossil fuels stimulated, in part, by governmental mandates and incentives. The regulatory environment has also motivated the search for carbon-neutral substitutes for petroleum-based lubricants. For example, the United States Department of Agriculture (USDA) has recently added crankcase oils to the bio-preferred program, which requires federal agencies and their contractors to give preferential treatment to lubricants containing more than 25% renewable content.1

The use of bio-based lubricants is not new and indeed some of the oldest lubricants used in industry were bio-esters sourced from plants.2 However, with the advent of the petroleum age, lubricant formulations came to depend on the superior properties of mineral base-oils obtained as a cut from some refineries.3 Today even superior properties are achieved with poly-α-olefins (PAOs) base-stocks produced by the cationic oligomerization/hydrogenation of ethylene-derived linear α-olefins (usually C10, Scheme 1).4 The PAO process is, however, environmentally unfriendly since it utilizes corrosive catalysts such as BF3, HF, or AlCl3. Moreover, the product distribution cannot be tightly controlled and it is quite common to get mixtures of dimers, trimers, and tetramers of 1-decene in the product mixture. Research efforts in homogeneous5 and heterogeneous6 catalysis have tried to overcome the selectivity and corrosivity issues; however, the discovery of an environment-friendly, efficient heterogeneous catalyst with high selectivity has proved elusive. As alternative to PAOs, we report here an entirely new class of lubricant base-oils exhibiting properties comparable to those of mineral oils and PAOs. The method of producing these base-oils features two-step approach involving a highly selective self-condensation of methyl ketones (MKs) and subsequent hydrodeoxygenation (Scheme 1). Several pathways are amenable for sourcing MKs (C8–C11) needed for this process from renewable feedstocks. For e.g., biomass-derived terminal alkenes serve as potential precursors which undergo alklylation7 with acetone or Wacker oxidation8 to produce requisite MKs. These alkenes can be sourced from the corresponding primary alcohols obtained from hydrogenation of triglycerides9 or Guerbet reaction10 of fermented alcohols. Alternatively, direct coupling of alcohols with acetone is also known to give MKs in moderate yields.11 In addition, biological routes have been developed to produce mid-/long-chain MKs directly from sugars.12 Other less-common approaches are listed in ESI.† In this report, we

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summarize our efforts to produce various lubricant base-oils starting from MKs, understand the structure–property relationship, and compare the properties of this new class of lubricants base-oils to those obtained via the PAO route.

Our procedure for the synthesis of lubricants builds on the self-condensation of \( n \)-alkyl methyl ketones (1) catalyzed by solid acids and bases (Table 1). The condensates produced are exclusively cyclic trimers the structures of which vary greatly with the nature of the catalyst. The condensation of 1 carried out in the presence of bases such as calcined hydrotalcite (MgAlO)\(^{14} \) results in a quantitative yield of 2a' and 2a'' (17 : 3) (entry 1, condition A). On the other hand, acid catalysts (e.g., Ta\(_2\)O\(_5\)/SBA-15)\(^{15} \) promote dehydration leading to the production of aromatic condensates (3a'/3a'' = 1 : 1 approx.) under nearly identical conditions (entry 2). The formation of trimer condensates 2 and 3 differ in the number of moles of water molecules released per mole of substrate at the end of the reaction (0.667 vs. 1), but involve the same, observable dimer condensates I and II as intermediates (Scheme 2).

To explain the observed intermediates and products, we propose the reaction pathways illustrated in Scheme 2. Methyl ketone 1 undergoes self-condensation to generate I and II promoted by a base or acid catalyst. The first step in the reaction sequence is the formation of the respective enolate/enol species (A–D). Subsequently, 1,2-/1,4-addition of A/B to I and II occurs in the presence of a base catalyst to generate intermediates III–V. On the other hand, acid catalysis proceeds exclusively through 1,2-addition of C/D to give VI. Finally, ring

### Table 1 Syntheses of various cycloalkane lubricant base-oils using the sequence of self-condensation and hydrogenation/hydrodeoxygenation

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ketone ([C_n])</th>
<th>Conditions A(^a)</th>
<th>Condensate ([C_{18}])</th>
<th>Conditions B(^b)</th>
<th>Cyclic alkane ([C_{18}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a ([C_6]) R(^1) = n-propyl</td>
<td>MgAlO(^{13,14} ), 160 °C, 3 h</td>
<td>2a ([C_{18}]) R(^1) = n-propyl</td>
<td>Pt/NbOPo(_4)^{14,15} H(_2) (3.45 MPa), 160 °C, 6 h</td>
<td>4a ([C_{18}]) R(^2) = n-propyl</td>
</tr>
<tr>
<td>2</td>
<td>1a ([C_6]) R(^1) = n-propyl</td>
<td>Ta(_2)O(_5)/SBA-15(^d), 200 °C, 24 h</td>
<td>3a R(^1) = n-propyl</td>
<td>Rh/C(_2), H(_2) (3.45 MPa), 200 °C, 16 h</td>
<td>5a R(^2) = n-propyl</td>
</tr>
<tr>
<td>3</td>
<td>1b–f ([C_6–C_{12}]) R(^1) = n-pentyl–n-nonyl</td>
<td>MgAlO(^{16} ), 160 °C, 6 h</td>
<td>2b–f ([C_{24}, C_{27}, C_{50}, C_{52}, C_{56}])</td>
<td>Pt/NbOPo(_4)^{14,15} H(_2) (3.45 MPa), 160 °C, 6 h</td>
<td>4b–f ([C_{24}, C_{27}, C_{50}, C_{52}, C_{56}]) R(^1) = n-pentyl–n-nonyl</td>
</tr>
<tr>
<td>4</td>
<td>1g ([C_{13}]) R(^1) = n-dodecyl</td>
<td>MgAlO(^{16} ), 160 °C, 12 h</td>
<td>2g ([C_{44}]) R(^1) = n-dodecyl</td>
<td>Pt/NbOPo(_4)^{14,15} H(_2) (3.45 MPa), 200 °C, 12 h</td>
<td>4g ([C_{44}]) R(^2) = n-dodecyl</td>
</tr>
<tr>
<td>5</td>
<td>1h ([C_{18}])</td>
<td>MgAlO(^{16} ), 160 °C, 12 h</td>
<td>2h ([C_{44}]) R(^1) = benzyl</td>
<td>Rh/C(_2), H(_2) (3.45 MPa), 120 °C, 6 h and then Pt/NbOPo(_4)^{14,15} H(_2) (3.45 MPa), 160 °C, 6 h and then</td>
<td>4h ([C_{44}]) R(^2) = c-hexylmethyl</td>
</tr>
<tr>
<td>6</td>
<td>1i ([C_{13}])</td>
<td>MgAlO(^{16} ), 160 °C, 16 h</td>
<td>2i ([C_{53}]) R(^1) = 2-ethylhexyl</td>
<td>Pt/NbOPo(_4)^{14,15} H(_2) (3.45 MPa), 160 °C, 6 h</td>
<td>4i ([C_{53}]) R(^2) = 2-ethylhexyl</td>
</tr>
<tr>
<td>7</td>
<td>1j ([C_6]) and 1k ([C_6])</td>
<td>MgAlO(^{16} ), 160 °C, 16 h</td>
<td>2j ([C_{45}]) R(^1) = furfuryl and</td>
<td>Pd/C(_2), H(_2) (2 MPa), 100 °C, 5 h and then Pt/NbOPo(_4)^{14,15} H(_2) (3.45 MPa), 220 °C, 6 h and then</td>
<td>4j (\cong 4b ([C_{45}]) R(^2) = n-pentyl–n-nonyl and 4k (\cong 4c ([C_{45}]) R(^2) = n-hexyl</td>
</tr>
<tr>
<td>8</td>
<td>1l ([C_{13}])</td>
<td>MgAlO(^{16} ), 190 °C, 16 h</td>
<td>2l ([C_{47}]) R(^1) = 2,2-bis(5-methyl furan-2-yl)ethyl</td>
<td>Pd/C(_2), H(_2) (2 MPa), 100 °C, 5 h and then Pt/NbOPo(_4)^{14,15} H(_2) (3.45 MPa), 220 °C, 6 h and then</td>
<td>4l ([C_{47}]) R(^2) = 2-pentylheptyl</td>
</tr>
<tr>
<td>9</td>
<td>1d ([C_{18}])</td>
<td>Ta(_2)O(_5)/SBA-15(^d), 230 °C, 24 h</td>
<td>3b ([C_{47}]) R(^1) = n-heptyl</td>
<td>Rh/C(_2), H(_2) (6.9 MPa), 200 °C, 24 h</td>
<td>5b ([C_{47}]) R(^2) = n-heptyl</td>
</tr>
</tbody>
</table>

\(^a\) Entries 1, 3–8 were carried out in a Dean–Stark separator; entries 2 and 9 were carried out in Parr reactor; toluene was used as solvent for entries 1–7, and 9; mixture of xylene was used as solvent for entry 8. \(^b\) Hydrogenations were carried out in a Parr reactor using octane as the solvent. \(^c\) 50 wt% of the catalyst with respect to substrate. \(^d\) 20 wt%. \(^e\) 0.2 mol% of the total metal content with respect to substrate. \(^f\) 0.25 mol%. \(^g\) 0.5 mol%. \(^h\) 0.2 mol%. \(^k\) 0.1 mol%. \(^l\) 0.2 mol%. MgAlO = calcined hydrotalcite.
closure of intermediates III–VI occurs either through cyclization or cyclodehydration to give products 2’, 2” and 3’, 3”. Formation of the kinetic enolate/enol intermediates (A and C) is highly favored due to steric/electronic factors and therefore the reaction proceeds predominantly via these intermediates rather than through the thermodynamic intermediates B and D.

Since synthetic PAOs used for lubricant formulations are primarily composed of C18 and C40 alkanes, we targeted the production of cyclic trimers containing 24–45 carbon atoms via condensation of biomass-derived Cn–C15 methyl ketones. The reaction conditions were optimized to enable the complete conversion of starting materials to trimers 2 and 3 (Table 1, conditions A). This condensation reaction is reversible and the retro-condensation is facilitated by water formed as a by-product of the reaction. To minimize this effect, we employed a Dean–Stark apparatus to continuously remove water from the reaction mixture. Using such an approach and MgAlO as the catalyst we were able to produce trimers (2) in near-quantitative yields (>98%) for n-alkyl (1b–g, Table 1, entries 3 and 4), branched alkyl (1i, entry 5), arylalkyl (1h, entry 6), and heteroaralkyl (1j–l, entries 7 and 8) methyl ketones as reactants. The time required for the completion of the reaction was directly proportional to the complexity of the alkyl substitution in 1 (entries 3–8). For example, the most complex ketone, 1l, required refluxing xylenes for completion (entry 8). As expected, the choice of catalyst also influenced the conditions required for the near-complete conversion of the reactants. For example, Ta2O5/SBA-15-catalyzed reactions required higher temperatures and longer times compared to MgAlO-catalyzed reactions for a given methyl ketone (entries 3 vs. 9). At this point, we thought about industrially relevant reactive distillation method as an alternative to Dean–Stark set-up to remove water by-product. Such a method would also eliminate the need for solvents during the reaction. In order to examine the efficiency of self-condensation in solvent-free conditions, 2-nonanone was heated with MgAlO catalyst under vacuum to facilitate water removal (see ESI† for details). The results indicated that the combined selectivity to 2c and 2c” is >95% even at an elevated temperature (190 °C). Usually, process optimization for industrial production would consider temperature and duration as important parameters. Here we show that increasing the process temperature allows us to reduce the residence time from 6 h (Table 1) to 90 minutes (Table S1†) while achieving high conversion (>90%) without any loss in selectivity.

Hydrogenation of the ketones 2 and alkyl benzenes 3 to the corresponding cyclic alkanes 4 and 5, is an essential step for obtaining hydrocarbon base-oils (Table 1, conditions B). Conversion of 2 to 4 can be accomplished in >98% yield using Pt/NbOPO3, a bifunctional catalyst that operates under mild conditions.16 Platinum catalyzes the reduction of the double bond functionalities of 2, whereas the acidic support (NbOPO3) facilitates the elimination of oxygen atoms. It is noted that condensates 2 and 3 possessing longer alkyl substituents required higher temperatures and longer reaction times for the complete reduction of the innermost double bonds (entries 3 vs. 4). The hydrodeoxygenations of furan-containing condensates 2f–l were also carried out at relatively high temperature (>200 °C). To avoid C–C bond scissions at high temperatures, Pd/C mediated saturation of the furan rings was conducted prior to hydrodeoxygenation (>95% yield for two steps, entries 7 and 8). Saturation of aromatic rings in 2h, 3a–b was accomplished by hydrogenation over Rh/C using condition B (Table 1, entries 2, 5, and 9, >98% yield). For aromatic compounds, the final hydrogenation step is not absolutely essential for producing lubricant base-oils. Alkyl benzenes are often added to lubricant formulations as they have acceptable properties as seen from Table 2, entry 12.

As seen from their structures, hydrocarbons 3–5 contain the appropriate number of carbons (C24–C45), but differ significantly in structure from known lubricant base-oils. While the synthetic PAOs are mainly branched alkanes, the compounds that we synthesized are exclusively aromatics (3) or cyclo-

\[
\text{Table 2 Evaluation of lubricant properties of cycloalkane base-oils}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cycloalkanes</th>
<th>KV100 a (cSt)</th>
<th>KV40 a (cSt)</th>
<th>VIb</th>
<th>PP c (°C)</th>
<th>DSC oxidation d (°C)</th>
<th>TGA Noack e (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4b (C26) R2 = n-pentyl</td>
<td>3.35</td>
<td>17.01</td>
<td>40</td>
<td>–69</td>
<td>224</td>
<td>58.3</td>
</tr>
<tr>
<td>2</td>
<td>4c (C27) R2 = n-hexyl</td>
<td>4.07</td>
<td>21.19</td>
<td>82</td>
<td>–66</td>
<td>224</td>
<td>21.6</td>
</tr>
<tr>
<td>3</td>
<td>4d (C30) R2 = n-heptyl</td>
<td>4.87</td>
<td>26.06</td>
<td>109</td>
<td>–72</td>
<td>224</td>
<td>7.5</td>
</tr>
<tr>
<td>4</td>
<td>4e (C31) R2 = n-octyl</td>
<td>5.72</td>
<td>31.57</td>
<td>123</td>
<td>–69</td>
<td>226</td>
<td>2.6</td>
</tr>
<tr>
<td>5</td>
<td>4f (C32) R2 = n-nonyl</td>
<td>6.55</td>
<td>37.18</td>
<td>131</td>
<td>–60</td>
<td>225</td>
<td>1.2</td>
</tr>
<tr>
<td>6</td>
<td>4g (C33) R2 = n-dodecyl</td>
<td>9.64</td>
<td>59.48</td>
<td>146</td>
<td>–9</td>
<td>229</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>4h (C36) R2 = c-hexylmethyl</td>
<td>Too viscous to analyse</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>4i (C33) R2 = 2-ethylhexyl</td>
<td>7.09</td>
<td>59.74</td>
<td>66</td>
<td>–54</td>
<td>212</td>
<td>22.5</td>
</tr>
<tr>
<td>9</td>
<td>4j ≡ 4b (C26) R2 = n-pentyl</td>
<td>3.51</td>
<td>18.11</td>
<td>49</td>
<td>–51</td>
<td>203</td>
<td>56.5</td>
</tr>
<tr>
<td>10</td>
<td>4k ≡ 4c (C27) R2 = n-hexyl</td>
<td>4.38</td>
<td>25.59</td>
<td>62</td>
<td>–63</td>
<td>210</td>
<td>30.4</td>
</tr>
<tr>
<td>11</td>
<td>4l (C31) R2 = 2-pentylheptyl</td>
<td>11.49</td>
<td>106.46</td>
<td>94</td>
<td>–51</td>
<td>212</td>
<td>1.7</td>
</tr>
<tr>
<td>12</td>
<td>3b (C30) R2 = n-octyl</td>
<td>4.29</td>
<td>20.07</td>
<td>121</td>
<td>–75</td>
<td>219</td>
<td>14.4</td>
</tr>
<tr>
<td>13</td>
<td>5b (C30) R2 = n-octyl</td>
<td>3.99</td>
<td>18.74</td>
<td>110</td>
<td>–57</td>
<td>222</td>
<td>26.6</td>
</tr>
<tr>
<td>14</td>
<td>Commercial C30 PAO</td>
<td>3.63</td>
<td>15.23</td>
<td>124</td>
<td>–72</td>
<td>221</td>
<td>9.6</td>
</tr>
</tbody>
</table>

hexanes (4 and 5). The lubricant properties of these compounds – the viscosity index (VI), pour point (PP), oxidation stability (DSC oxidation), and volatility (TGA Noack) – were evaluated according to ASTM standards (Table 2). We also explored the structure-property relationship by studying a number of different analogues with varying functionality around the cyclohexane core. A steady increase in the VI of 4b through 4g (Table 2, entries 1–6 and Fig. 1) indicates that the viscosity change with temperature decreases as the length of the linear alkyl substitution increases. Higher analogues of this series of compounds (C_{33}+) possess an excellent VI compared to that of petroleum-derived C_{30}PAO (entry 14).

In general, the measured kinematic viscosities of cyclic alkanes at reference temperatures (40 °C and 100 °C) are higher than those of the corresponding acyclic, branched alkanes (entries 3 vs. 14). The viscous nature of the cyclic compounds is highly evident when the alkyl side chain of 4 contains additional cyclohexane functionalities (4h, entry 7). However, the presence of the cyclohexane core improved the pour points of most analogues to <-60 °C. We also found that longer alkyl chain substitution in 4g resulted in a poor pour point due to alkyl chain stacking, similar to that found in waxes. While the oxidation stabilities of the cyclic compounds are comparable to each other and to that of commercial C_{30}PAO, the volatilities are inversely proportional to the molecular weights within the subset of 4b–g (Table 2, entries 1–6 and Fig. 1). 4g turned out to be the least volatile lubricant and exhibited a high VI; however, the pour point for this compound was also quite high. Of all the compounds analyzed, 4e and 4f contained the best overall lubricant properties consistent with those currently used in the transportation sector.

The branched alkyl substituted cyclohexane 4i exhibited higher viscosities but a lower VI than that of the corresponding linear alkyl substituted isomer 4c (entries 4 vs. 8). This is a consequence of the high dependence of viscosity on temperature attributable to excessive branching of the molecular structure. Notably, the volatility of 4i is exceptionally high (~10 fold) compared to that of 4c due to decreased intermolecular interactions caused by increased branching. The properties of the structurally similar lubricants 4b, 4c and 4j, 4k derived from alkyl and furanic precursors, respectively, were comparable (entries 1, 2 and 9, 10). Due to the high viscosities associated with 2-methylfuran-derived lubricant, 4l may be better suited for industrial applications such as in wind turbines and compressors, rather than for automotive use. Aromatic C_{30} lubricant 3b and the corresponding cyclohexane analogue 5b have good viscosity indices, pour points and oxidation stabilities, but poor volatilities compared to those of commercial C_{30}PAO (entries 12–14). A comparison of volatilities of various C_{30} base-oils (entries 3, 7, and 12–14) suggests that this property does not depend on the molecular weight alone but involves other functionalities present in the molecular structure.

In conclusion, we have developed a strategy for the highly selective trimORIZATION of methyl ketones to produce bio-lubricants. The alkyl and furan-containing ketones required for this process can be conveniently obtained from biomass and the metal oxide catalysts employed are non-corrosive solids (e.g., MgAlO). The cyclic alkane lubricants derived from this method possess excellent pour points, viscosity indices, and oxidation stabilities which are comparable to those of conventional synthetic lubricants. A systematic structure–property relationship study indicated that the viscosity index of these materials increases steadily with length of alkyl side chain. Conversely, the volatility of these compounds exhibits an inverse dependence on alkyl chain length. Such relationships are valuable for directing future research aimed at developing renewable lubricants.

**Experimental**

General procedure for MgAlO-catalyzed self-condensation of ketones: a solution of 1 (20 g) in toluene (200 mL) was added with MgAlO (20 g) in a 500 mL round bottom flask equipped with a magnetic spin bar. The flask was then attached to the Dean–Stark apparatus and refluxed with stirring (800 rpm) in a pre-heated oil bath at conditions A given in Table 1. A collection of by-product water was observed in the side-arm of the apparatus during the course of the reaction. The product mixture was then cooled to room temperature and filtered through a fritted funnel by washing the catalyst using ethyl acetate (3 × 100 mL). The products (2) in the filtrate were recovered after evaporation of the solvents and used for the next step without further purification.

General procedure for hydrodeoxygenation of condensates: a solution of 2 (5 mmol) was added with respective hydrogenation catalysts (metal loadings are calculated with respect to 2) in a 25 mL Parr reactor vessel. Octane (5 mL) was added to reduce the viscosity and ensure good mixing in the Parr reactor during the reaction. The reactor was sealed, flushed with nitrogen gas (2×), hydrogen gas (3×) and subsequently charged with the required pressure of hydrogen gas. The Parr reactor was stirred at 500 rpm and subjected to respective conditions mentioned in Table 1, conditions B. The reaction mixture was then cooled to room temperature and filtered through a fritted funnel using hexanes as a washing solvent (3 × 20 mL) to remove the catalyst. The filtrate was concentrated under reduced pressure to recover cyclic alkanes 4.

**Fig. 1** Variations in the properties of lubricant base-oils depending on the number of carbon atoms in the linear side chains 4b–g.
Acknowledgements

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Notes and references

1 R. Buckhalt, in Society of Tribologists and Lubrication Engineers, 2014.