A Critical View on Catalytic Pyrolysis of Biomass

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The rapid heating of biomass in an oxygen-free environment optimizes the yield of fast-pyrolysis liquids. This liquid comprises a mix of acids, (dehydrated) carbohydrates, aldehydes, ketones, lignin fragments, aromatics, and alcohols, limiting its use. Deoxygenation of these liquids to replace hydrocarbons represents significant challenges. Catalytic pyrolysis is seen as a promising route to yield liquids with a higher quality. In this paper, literature data on catalytic fast pyrolysis of biomass are reviewed and deoxygenation results correlated with the overall carbon yield. Evidence is given that in an initial stage of the catalytic process reactive components are converted to coke, gas, and water, and only to a limited extent to a liquid product. Catalysts are not yet good enough, and an appropriate combination of pyrolysis conditions, reactive products formed, and different reactions to take place to yield improved quality liquids may be practically impossible.

1. Introduction

Fast pyrolysis is the rapid heating of biomass in an oxygen-free environment to optimize the yield of liquids. It offers a rapid and efficient means to depolymerize lignocellulosic biomass. Among the primary thermochemical conversion routes, fast pyrolysis is one of the most economically feasible ways to convert biomass into liquids, and has, therefore, attracted a lot of interest in the past two decades. Unfortunately, the liquid product contains a significant amount of reactive, oxygenated species and is a mix of organic acids, (dehydrated) carbohydrates, aldehydes, ketones, (depolymerized) lignin fragments, aromatics, and alcohols. For that reason the use of these liquids is up to now limited to combustion, and in the future likely gasification.

If the liquid is to be used in other applications, specifically to replace hydrocarbons, these reactive oxygenates—precursors for gas and coke—represent significant challenges. Removal of these oxygenates requires catalysts, and processes investigated include the use of catalysts directly in the pyrolysis step (in situ), either in-bed when catalysts are used in the fast pyrolysis process itself or ex-bed in case a reactor is connected to the pyrolysis process, to convert the non-condensed pyrolysis vapor. Herein, the in-bed and ex-bed options are referred to as indicated in Figure 1.

For more than three decades catalytic pyrolysis has been seen as one of the most promising routes to yield liquids with a better quality than the “original” pyrolysis liquids, where quality is usually related to a (substantially) lower oxygen content. It seems that in particular Mobil’s MTG process—converting methanol to gasoline over ZSM5-type catalysts—inspired researchers. Use of catalysts in fast pyrolysis reportedly has high potential, as it enables the production of hydrocarbons directly from biomass or liquids with higher quality than the conventional in relation to its use in subsequent (upgrading) processes. The clear advantage is an integrated process, in which re-evaporation of the liquids can be avoided. A purely theoretical, but commonly referenced, equation for the oxygen removal to yield (aromatic) liquids, CO2, and water, amongst others, is provided by Bridgwater:[1]

\[
C_6H_8O_4 \rightarrow 4.6 \text{CH}_3 \text{J}_2 + 1.4 \text{CO}_2 + 1.2 \text{H}_2\text{O}
\]  

(1)

Coke formation is neglected and all carbon loss is reflected only as CO2, yielding a theoretical yield of 42 wt% and an energetic yield (HHV) of near 100% [see also Eq. (4)].

The earliest reference may be the Occidental Research Corporation process, in which pyrolysis vapors are passed over ZSM5.[2] In Europe, a first project started in 1995 with the objective to produce higher quality oils from biomass through catalytic pyrolysis (JOR CT95-0081). This project was followed by “Biocat” (ENK6-CT-2001-00510) in the period of 2001–2005. In hindsight, measurable objectives were absent or unclear, and analysis protocols not standardized. Surprisingly, even elemental analysis of liquids (including oxygen) was not carried out routinely, but instead the deoxygenation was related to CO2 production. In both these projects, the use of catalysts in the pyrolysis process resulted in significant lower carbon

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yields, with a sometimes substantial lower oxygen level in the liquid. However, no significant breakthrough was obtained in the area of catalyst or process development.

In the period 2001–2007 (catalytic) pyrolysis was of less interest for industries, government, and researchers due to possibilities to use vegetable oils and sugars for the production of first-generation transportation fuels. Since 2007, when petroleum prices increased and the interest in second-generation fuels increased, a revival is noted in pyrolysis in general (and specifically catalytic pyrolysis). Since then a growing number of universities, research institutes, and organizations are again working on the development of catalytic pyrolysis technology, justified by the possibility that the product is compatible with petroleum feedstocks or that aromatics [benzene, toluene, and xylene (BTX)] can be produced in sufficient yields. In Europe and the US, various projects are ongoing, possibly inspired by the claims made by the company KiOR.

In 2010, ground breaking activities in catalytic pyrolysis were announced by KiOR, a joint venture of Khosla Ventures (KV) and the Dutch BioeCON, reporting the construction of a 500 BDT day\(^{-1}\) (BDT = bone-dry ton) commercial production unit (approx. 40000 t per year fuel). The technology was based on the idea of oxygen removal by fluid catalytic cracking (FCC)-derived catalysts in a modified fluid catalytic cracker. The R&D behind KiOR was initiated by BioeCON in 2006–2007, suggesting the impregnation of biomass with salts to reduce the cracking temperature. Its activities included involvement of researchers from Spain, Greece, USA, and The Netherlands. In 2012, the construction of the Columbus plant based on a new concept was completed, but the excitement was only for a rather short moment; in May 2014, KiOR’s facility was brought to a safe, idle state\(^{[7]}\) and in November 2014, the company filed for bankruptcy.

These developments justify a critical review of literature data on the yields obtained in the catalytic pyrolysis of biomass. Several reviews have been prepared in the last few years on types of catalysts and reactor systems applied, but none so far actually focused on the liquids yield in relation to the quality. The present paper aims to provide a first approach to analyze the existing experimental literature data related to yield and deoxygenation, and will provide recommendations for future work to improve tools. This includes suggestion for a minimum of analysis data to be reported in scientific publications.

2. Review of Literature Data

During the last years, a proliferation can be noticed in articles and papers published on catalytic pyrolysis of biomass. Scifinder, a leading scientific database of nearly 2500 journals and 26000 books, lists a total of over 11000 papers related to a combination of key words ‘catalytic’, ‘pyrolysis’, and ‘biomass’. Over 1600 were published in 2014 compared to a total of 736 for the total period before 1995, which shows the increasing interest of researchers in catalytic pyrolysis. This trend is further illustrated in Figure 2, in which the number of publications is presented as a function of the year of publication. In the last year, a few reviews have been prepared on catalytic pyrolysis.

The information provided in most of these papers is usually restricted to the effects of the catalyst, the product yields, sometimes providing elemental contents, but, in general, limited or no specific details are presented on the product characteristics (viscosity, molecular weights, its tendency to char, and so on) to justify the better quality. In most of these papers a common assumption is that the oxygen content of the liquid is directly related to its quality, thus justifying the use of catalyst in the fast pyrolysis, but, surprisingly, information on the oxygen content in the oil is not always provided. \(^{[8d]}\)

Besides, oxygen reduction in itself cannot be the only single criterion: methanol and ethanol contain 50 and 25 wt % oxygen, respectively, and both fuels are regarded as high value (and quality).

Clearly, the oxygen content in the oil provides some clues to the quality of the liquid, but it should be looked at very carefully. Partial polymerization of pyrolysis liquids effectively lowers the oxygen content, but also yields a very viscous (sometimes even solid) product. As important, oxygen reduction comes with a (high) price. Herein, it will be demonstrated that the overall biomass-to-liquid carbon yield is directly relat-

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ed to the oxygen reduction. The carbon yield \( \eta_C \) is defined by the moles of carbon in the feed that is retained in the preferred (organic) product. The actual oxygen reduction \( \xi_o \) is based on the oxygen content compared with that obtained by a thermal reaction only. These two parameters are defined as follows:

\[
\xi_o = \left( 1 - \frac{O_{\text{oil, daf}}}{O_{\text{thermal oil, daf}}} \right) \cdot 100 \%
\]

\[
\eta_C = \left( \frac{n_{C, \text{oil, daf}}}{n_{C, \text{feed, daf}}} \right) \cdot 100 \%
\]

(2)

where \( n_{C, \text{feed, daf}} \) represents the moles of carbon in the feed and \( O_{\text{oil, daf}} \) is the oxygen content of the liquids produced over a catalyst, and \( O_{\text{thermal oil, daf}} \) the oxygen content reported by the authors for the liquids derived in an uncatalyzed fast pyrolysis run. All data are provided on a dry-ash-free basis (daf). Clearly, the carbon yield can also be calculated on basis of the uncatalyzed oil as well as the oxygen reduction on basis of the feed; however, similar conclusions to the ones presented below will be obtained. It must be noted that the definition for the deoxygenation rate here is different from the one recently proposed, in which it is related to the absolute number of oxygen mol retained in the liquid.\(^{[9]}\) This latter definition is rather trivial as very low bio-oil yields present in the aqueous phase are neglected. Addition of these oxygenates to the liquids will increase the carbon yield but also reduces the overall deoxygenation rate.

Figure 3. Compilation of literature data for the deoxygenation of biomass-derived liquids in catalytic pyrolysis processes, with the oxygen reduction related to the oxygen content of uncatalyzed oil and the carbon yield, represented by the ratio between the amount of carbon in the liquid products and the carbon in the biomass, see Equation (2): the solid lines given are calculated on basis of Equations (1), (5), and (6) whereas the broken lines represent isoenergetic lines calculated from Equation (3).

2.1. Biomass catalytic pyrolysis

From the wealth of publications provided by ScienceDirect, only a few provide sufficient information on the residual oxygen content and related overall carbon yield. In Table 1 these references, further restricted to the use of woody biomass as a feed, are summarized, from which the respective figures have been constructed. A typical plot that effectively shows the relation between \( \xi_o \) and \( \eta_C \) is presented in Figure 3. For a large variety of catalysts, temperatures, processes, and process conditions, it suggests that there are two distinct regions: a region I, where the carbon yield is drastically reduced while the oxygen content remains relatively high (mild deoxygenation), and a region II where substantial deoxygenation is possible at the expense of carbon (severe deoxygenation). The results are rather consistent, but some remarks can be made:

- The data presented are rather conservative as in most cases only the yields and oxygen contents of the organic products have been reported and the (usually oxygenated) organics present in the aqueous phase are neglected. Addition of these oxygenates to the liquids will increase the carbon yield but also reduces the overall deoxygenation rate.

- Data considered are taken irrespective of catalyst type, operating conditions, catalyst-to-oil ratios, biomass feed type, reactor type (ex-bed or in situ), and so on. A further division in these individual parameters results in an even more distinct pattern, but, for the sake of simplicity, will not be taken into account here.

To estimate the carbon loss in terms of energy, Figure 3 also shows the so-called ‘isoenergetic’ curves. These dashed curves represent the theoretically energetic yields (\( \eta_o \)) of 10\%, 25\%, 50\%, 75\%, and 100\% efficiency, defined by the energetic value of the liquid product divided by the energetic value of the feed material, both heating values arbitrarily defined by the higher heating value:

\[
\eta_o = \left( 1 - \frac{\text{HHV}_{\text{oil, daf}}}{\text{HHV}_{\text{feed, daf}}} \right) \cdot 100 \%
\]

(3)

For simplicity, the HHV value here is calculated by the Milne equation [Eq. (4)]\(^{[1]}\) neglecting ash, sulfur, and nitrogen content:
Table 1. References for the catalytic pyrolysis.\[a\]

<table>
<thead>
<tr>
<th>Bed material</th>
<th>Feed</th>
<th>Temperature [°C]</th>
<th>Reactor system</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM5</td>
<td>pine</td>
<td>500–650</td>
<td>IB: 4&quot; ID BFB</td>
<td>continuous addition and withdrawal catalyst; complete deoxygenation aimed at BTX production; low overall carbon yield</td>
</tr>
<tr>
<td>ZSM5</td>
<td>corn cob</td>
<td>thermal: 400–700</td>
<td>catalytic: 550</td>
<td>IB: 30 mm ID BFB</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>IB: BFB</td>
<td>oxygen level in liquids are not reported; hydropyrolysis; low BTX yields (&lt; 6%)</td>
</tr>
<tr>
<td>NiMo/Al2O3, (sulfided)CoMo/ Al2O3, alumina, silica</td>
<td>pine, spruce, tropical lauan</td>
<td>500–660</td>
<td>IB: BFB</td>
<td>water levels in the oil are not reported; not clear if data are reported on as received basis</td>
</tr>
<tr>
<td>ZSM5; sand, calcite, dolomite</td>
<td>sawdust</td>
<td>BFB: 450–550</td>
<td>EB: BFB + PB</td>
<td>packed bed pyrolysis followed by packed bed catalytic upgrading</td>
</tr>
<tr>
<td>ZSM5; sand</td>
<td>switchgrass</td>
<td>600</td>
<td>IB: Auger</td>
<td>packed bed pyrolysis followed by packed bed catalytic upgrading</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>IB: CB, BFB</td>
<td>packed bed pyrolysis followed by packed bed catalytic upgrading</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>oxygen thermal not provided; estimated oxygen content 37 wt %</td>
</tr>
<tr>
<td>ZSM5</td>
<td>aqueous phase</td>
<td>405–555</td>
<td>IB: 10 mm ID PB</td>
<td>packed bed pyrolysis followed by packed bed catalytic upgrading</td>
</tr>
<tr>
<td>ZSM5 (and modified with Mo, Co)</td>
<td>Lignocell HBS 150-500</td>
<td>pyrolysis: 500</td>
<td>IB: CB</td>
<td>packed bed pyrolysis followed by packed bed catalytic upgrading</td>
</tr>
<tr>
<td></td>
<td></td>
<td>regen.: 650</td>
<td></td>
<td>packed bed pyrolysis followed by packed bed catalytic upgrading</td>
</tr>
<tr>
<td>ZSM5, MgO, NiO, alumina, Zr–Ti</td>
<td>Lignocell HBS 150–500</td>
<td>pyrolysis: 500</td>
<td>EB: 2 PB in series</td>
<td>packed bed pyrolysis followed by packed bed catalytic upgrading</td>
</tr>
<tr>
<td>Zs, Ti, SAI</td>
<td>poplar</td>
<td>450</td>
<td>IB: 50 mm ID BFB</td>
<td>addition steam in reaction S/B varied in thermal exp. from 0-0.67 kg\textsubscript{steam} kg\textsubscript{biomass} /C\textsubscript{0}\textsuperscript{1}; catalytic deoxygenation due to dehydration</td>
</tr>
<tr>
<td>ZSM5; sand; silica (modified with Ni,V); ZSM5/bentonite (modified with Ni,V)</td>
<td>mixture of pine and spruce</td>
<td>thermal: 400–550</td>
<td>IB: 72 mm ID BFB</td>
<td>two staged: pyrolysis vapors were fed over a packed bed with catalyst</td>
</tr>
<tr>
<td>ZSM5 (H and Na), Y-zeolite, alumina, SS</td>
<td>wood mixture</td>
<td>pyrolysis: 500</td>
<td>EB: 100 mm ID BFB; 100 mm PB</td>
<td>oxygen content estimated from product distribution; WHSV: 1.8 and 3.6 h\textsuperscript{-1} experiments with regeneration carried out</td>
</tr>
<tr>
<td>ZSM5, mordenite, Y-zeolite, silicatel, Si-Al</td>
<td>pyrolysis liquid (Ensyn)</td>
<td>catalyst bed: 500</td>
<td>PB</td>
<td></td>
</tr>
<tr>
<td>Y-zeolite (K, M)</td>
<td>white oak</td>
<td>500 and regen.</td>
<td>IB: 76 mm BFB</td>
<td></td>
</tr>
<tr>
<td>Ru/TiO\textsubscript{2}</td>
<td>oak; switchgrass</td>
<td>500</td>
<td>EB: 24 mm ID; pyrolysis reactor + PB</td>
<td></td>
</tr>
<tr>
<td>Fe-impregnated mesoporous silica-alumina</td>
<td>pyrolysis liquid</td>
<td>450</td>
<td>PB</td>
<td></td>
</tr>
<tr>
<td>H-ZSM5</td>
<td>pine</td>
<td>pyrolysis: 450–550</td>
<td>EB: BFB + PB</td>
<td></td>
</tr>
</tbody>
</table>

\[a\] IB = in-bed; EB = ex-bed. PB = packed bed; BFB = bubbling fluid bed; CFB = circulating fluid bed; ID = inner diameter; SS = stainless steel; SB = steam-to-biomass ratio; WHSV = space velocity defined by \text{kg\textsubscript{oil} h\textsuperscript{-1}} / \text{kg\textsubscript{catalyst} h\textsuperscript{-1}}.
HHV_{i} = (0.341 \text{ wt }\%_{\text{C}} + 1.322 \text{ wt }\%_{\text{H}} - 0.12 \text{ wt }\%_{\text{O}}) \cdot 100 \quad (4)

In these isenergetic calculations, the carbon content of the liquid produced is taken as the balance, as the oxygen is given by the deoxygenation rate and the hydrogen content is assumed. As a first simplification, the hydrogen content is taken linearly with the conversion of the biomass, from 6.2 wt% for zero conversion to 11.5 wt% in a fully deoxygenated product. This level is rather arbitrary, but simple calculations show that other values (from 6 to 10 wt%) or a hydrogen content increasing linearly with a decreasing oxygen content do not have major effects on the overall trends of the curves.

In Figure 3, three additional curves are presented. The first one is the theoretical curve provided by Equation (1), where deoxygenation is presumably taking place linearly, ranging from 0 to 100% conversion. The theoretical curve closely follows the curve for $\eta_{c} = 100\%$. Clearly, the thus calculated carbon yields do not come close to any of the experimental data points. The experimental yields are much lower, specifically as carbon and gas yields are much higher: an optimistic case is presented by Equation (5), constructed by addressing the experimental yields for the carbon and the ratio between CO$_{2}$ and H$_2$O:

$$C_{6}H_{8}O_{4} \rightarrow (1-x) C_{6}H_{4}O_{4} + x (CH_{1.8} + 0.45 CO_{2} + 3.1 H_{2}O + 4.55 C) \quad (5)$$

Here, $x$ represents the biomass conversion, ranging from 0 to 1.

Clearly, also Equation (5) overestimates the carbon yield. A lower trend line can be predicted only if it is assumed that a significant part (here 65%) of the biomass is instantaneously converted to carbon and water (and does not take place in any further reaction), while the remaining 35% is converted according to Equation (5). Overall, Equation (6) can be constructed in Figure 3 for 0 < $x$ < 1:

$$C_{6}H_{8}O_{4} \rightarrow (3.9 \text{C} + 2.6 \text{H}_{2}\text{O}) + 0.35 C_{6}H_{4}O_{4} \rightarrow (3.9 \text{C} + 2.6 \text{H}_{2}\text{O}) + 0.35 (1-x) C_{6}H_{4}O_{4} + x (0.14 \text{CH}_{1.8} + 0.07 \text{CO}_{2} + 1.3 \text{H}_{2}\text{O} + 1.9 \text{C}) \quad (6)$$

In the ideal case, deoxygenation in the catalytic pyrolysis occurs though removal of CO$_{2}$ and H$_2$O, as a result of which most of the hydrogen and carbon is retained in the liquid. In Figure 3, this case would have been reflected by a low carbon loss at a high deoxygenation rate [see Eq. (1) for oxygen removal by CO$_{2}$ and H$_2$O], and a steep slope in the deoxygenation line. The reality, however, is a worst-case scenario, namely an initially high carbon loss associated with low deoxygenation rates. The two boundaries in this plot are (i) uncatalyzed pyrolysis ($\eta_{c}, \xi_{d} = (65\%; 0\%)$, and (ii) full deoxygenation ($\eta_{c}, \xi_{d} = (15\%; 100\%)$). Depending on the process severity (defined by the deoxygenation rate), carbon yields for liquids with oxygen contents < 10 wt% (or 75 wt% reduction) are well below 25 wt%. To retain higher carbon yields in the liquids, less deoxygenation is thus allowed, the latter usually associated with similar or worse product properties compared to the original pyrolysis liquids (such as high viscosity, residual water, high acid number, and alkali).

This general conclusion from the data points in Figure 3 is not new or very surprising; already in the nineties, an extensive set of data was provided for a two-staged catalytic pyrolysis process of biomass. In papers by Williams and Horne (1994–1996), pyrolysis vapors were produced in fluid beds without catalyst, and further conversion of the vapors took place over a packed bed catalyst[12]. Data for the catalytic conversion of pyrolysis liquids over FCC or zeolite catalysts were published around the same time by Adjaye et al. (1995).[13] The organic yields for the catalytic pyrolysis of biomass over acidic conventional FCC catalysts are far less than 20 wt%[14] whereas some minimal optimization could be achieved by varying the actual process conditions. The patterns shown in Figure 3 have not been presented elsewhere yet, but trends can be concluded from the early experiments of Williams and Horne. For the sake of clarity, these are separately presented in Figure 4. Again, the oxygen reduction and carbon yield are based on the ratio between product and feed obtained by thermal processing. The curve trend is convincing: an initially high carbon loss is associated with low deoxygenation rates, while the preferred deoxygenation step occurs when most of the carbon is already converted into less valuable products, gas, and char. Trends are indicated by solid lines similar to Figure 3, and apparently the low efficiency trend line is followed, with resulting biomass-to-liquid carbon yields even less optimistic than that provided for the data in Figure 3.

In addition to the negative trend of deoxygenation versus carbon yield, it is also apparent that most literature data show a relatively high residual oxygen content, on the order of 10–20 wt%. Only in a few cases complete deoxygenation is indeed achieved. Supposedly, only if fresh and very reactive catalysts are applied, and at relatively severe operating conditions, oxygen contents < 1 wt% are reached. In practical applications, a so-called ’spent’ catalyst will be used, which is a catalyst regenerated by burning off the coke. This spent catalyst is usually less active than the fresh one, even more so as the ash from biomass can quickly affect the catalyst’s structure and composition. Full deoxygenation in the catalytic pyrolysis during continuous operation is not likely[16]

Values obtained by KiOR in large-scale processing are not published in the open literature, but a recent patent application by KiOR aims at hydrotreating processes using feedstocks with a residual oxygen content of up to 18 wt%[16], suggesting that the residual oxygen contents in the commercial BFCC is around that value. These oxygenates probably include residual phenols (typically 10–30 wt% oxygen), which are much more recalcitrant to deoxygenation and require severe conditions.

It is postulated that in an initial stage of the process the most reactive components are converted to coke (with associated gas and water) and only to a limited extent to the preferred liquid products. It is likely that these highly reactive components are or at least include the (dehydrated) carbohydrates in the case of a pyrolysis liquid and (homo-)cellulose-derived fragments when solid biomass is fed as these carbohy-
drates are the least stable. At the increased reaction severities (reflected by the higher oxygen reduction levels) cracking of (some of) the more stable components, and likely the lignin fraction, is taking place, eventually yielding hydrocarbons. The latter usually contains a larger BTX fraction. 

Liquids from thermal pyrolysis already experienced a cracking step but also contain significant amounts of (dehydrated) carbohydrates. It is interesting to note what occurs if these liquids are further cracked over zeolite, and data for the conversion of pyrolysis liquids over a variety of catalysts in packed bed were tabulated. It is interesting in these experiments that the conversion of the liquids could be carried out at rather low temperatures (290–410 °C). The data are summarized in Figure 5, following the same methodology as in Figures 3 and 4. Although these researchers did not provide information on the elemental composition of the produced liquids, rough but rather reliable estimates can be estimated from the overall product distribution (assuming that acids are acetic acid, aromatics have a carbon-to-hydrogen ratio of 1, and so on). For the overall carbon yield (biomass-to-liquid), a carbon yield of 70% has been assumed in the prior pyrolysis step (weight yields from biomass to liquids were 74%).

Again, similar trends as for biomass are observed, with overall biomass-to-liquid carbon yields well below 30 wt% at a quest for a better catalytic process, steam pyrolysis in the presence of catalyst is applied, suggesting that steam affects the yield and composition and promotes the oxygen removal from the liquid. These data are not included in Figures 3–5, but for a better comparison, are separately plotted in Figure 6. The solid symbols represent catalytic pyrolysis of biomass under steam pyrolysis conditions whereas open symbols are used for the uncatalyzed runs. The plot indeed shows a high carbon yield related to a significant deoxygenation rate, and one might conclude that it offers serious potential. Remarkably, however, the results of the uncatalyzed experiments almost perfectly coincide with those rather low deoxygenation rates. Clearly, molecular structures are present in the liquid similar to those originally in the biomass, providing indirect proof that during the fast pyrolysis the products are trapped before thermodynamic equilibria can be reached.

Figures 3–5 show that zeolite catalysts (and specifically the fresh ZSM5 ones) are too reactive to selectively convert such oxygenated materials, and the alternative is to apply lower temperatures and/or (much) lower amounts of reactive catalyst material. In case of biomass, temperatures over 400 °C are essential to break down the solid structure, and lowering the temperature is not an option. In...
of the catalytic experiment, suggesting that catalysis does not play a significant role. The catalyst seems essentially inactive. Apparently, a different mechanism plays a role compared to that of the zeolite catalysts. This mechanism is dehydration instead of a preferred decarboxylation. Generally, dehydration leads to products with high viscosity, large molecular weight, and an oil quality even less than that of the uncatalyzed pyrolysis liquids. Unfortunately, not enough information is provided by the researchers to justify the approach as a lower-viscosity oil is obtained; average molecular weights presented, however, suggest that severe polymerization occurred.  

3. Discussion and Further Outlook

The results presented in the literature do not provide ample evidence that on a micro, meso and macro level, catalytic pyrolysis provides sufficient benefits compared with uncatalyzed fast pyrolysis. On a catalyst level, the most likely primary mechanism taking place is the formation of coke on the very active catalyst surface before any other reaction leading to hydrocarbons can take place. Coke defined here is the carbon deposited on the catalysts and is different from the carbon-containing solid char particles derived after pyrolysis of biomass. The gases evolved from these coking reactions are further reacted with the catalyst surface to potentially form (partly) deoxygenated compounds. As an overall reaction, dehydration is observed, a reaction promoted by the high temperatures and acidic catalyst surface. This can be further elucidated by comparing the O/C and the H/C ratios of the catalytic pyrolysis liquids.  

To take into account the variety of feeds used, the ratios of O/H and H/C for the catalytic pyrolysis liquid and the uncatalyzed experiment, respectively, are used here (see Figure 7). Although the data are rather scattered in most of the publications, a common trend is noted, namely that the decrease in the O/C versus the H/C ratios follows the dehydration slope. This is more clearly noted for the data generated using one catalyst under different conditions and less for the papers where different catalyst are applied (for example Stefanidis et al., 2011 [19]). For comparison, the results in Figure 7 for the individual papers are plotted in Figure 8.  

In most cases, the H/C ratio for the catalytic oil is substantially higher than expected on the basis of the dehydration line, which, as no hydrogen is fed to the system, which means that carbon rejection is significant as no hydrogen is fed to the
system. Together with the low overall carbon yield at low de-
oxidation rates (thus limited CO\textsubscript{2} formation), this clearly points to carbon rejection by formation of coke—char. Considering the many reactions that can take place at different temperature levels for the various oxygenates, it is fair to postulate that the catalysts so far tested in catalytic pyrolysis (apart from catalyst stability and effects of biomass contaminants) are not selective enough to steer towards either the preferred reactions (the latter include decarboxylation, cracking, aromatization, and alike).

Removal of carbon through decarboxylation might indeed take place (as is noted by high CO\textsubscript{2} yields reported in all literature references), but, (i) not to the extent one wishes to obtain, (ii) probably only at the initial stage of the pyrolysis process, (iii) not at the temperature range the catalysts are supposedly active, and (iv) at a rate lower than removal of carbon as coke.

On the product side, catalytic pyrolysis can clearly yield liquids with oxygen contents lower than those of the conventional uncatalyzed pyrolysis liquids. However, and contrary to what is expected from general literature reviews, only in a few cases is full deoxygenation of the liquid indeed experimentally obtained, and the general view on the use of catalytic pyrolysis for the production of oxygen-free liquids may be overly optimistic. The data summarized in Figures 3 and 4 suggest a maximum value for $\chi\textsubscript{O}$ of around 75%, with only two publications referring to full deoxygenated liquids. This deoxygenation rate corresponds with a residual oxygen content in the liquid of near 10 wt%, a value that might allow further refining without substantial problems. This unfortunately comes at the expense of carbon, and carbon yields (from biomass to liquid) between only 10 and 20 wt% are realistic. More than 80% of the carbon fed is thus converted in a less valuable by-product (gas, char, coke), in practice probably to be combusted (or gasified). In case of a less active catalyst (and in the presence of steam), higher carbon yields are obtained, and the products have a lower oxygen content. In the latter case, it is not clear whether the products obtained are of better quality than the thermally produced oils or are similar to oils derived from pyrolysis by dehydration (for example at high temperatures and pressures\textsuperscript{[20]}).

However, the oxygen content of the liquid is not per se a measure for the quality of the liquids. Upon deoxygenation of liquids through dehydration, substantial amounts of oxygen can be removed, but the viscosity of the liquids increases dra-

Figure 8. Comparison of O/C and H/C ratios for catalytically derived pyrolysis liquids. For the data see the legend in Figure 7.
matically as in case of such a thermal treatment. This is almost certainly the case in the steam pyrolysis experiments listed in Figure 3 and this might in general be true for any liquid product prepared through catalytic pyrolysis. The oxygen content, if not removed below 10–15 wt %, might not be the key performance indicator to look for in the development of catalysts.

Although carbohydrates can be converted into hydrocarbons,[21] a certain extent of oxygen defunctionalization should be aimed at, specifically in the case of carbohydrate(s). At the same time, this defunctionalization should occur while retaining the potentially high overall carbon yield of uncatalyzed pyrolysis. These objectives pose sufficient challenges in itself, as very reactive carbohydrate fractions formed in the pyrolysis reaction (and present in the produced pyrolysis liquids) must be selectively converted at the high temperatures required to crack the biomass. The following additional objectives are considered important but less so as they could also be obtained in subsequent processing:

- Reducing the (average) molecular weight (to an estimated 200–500 Da region);
- Reducing the water content (<10 wt %, by reducing the polarity of the liquids), and
- Increasing the high H/C ratio.

It is likely that less active catalysts in combination with less severe process conditions are required that reduce the carbon loss while allowing a large enough oxygen reduction to be beneficial in further processing. The catalysts studied in literature, including solid acids (FCC, zeolites, silica–alumina, alumina, etc.), metal oxides (such as zinc oxide, zirconia, ceria, and copper chromite), and other inorganic materials (alkali, metal chlorides/phosphates/sulfates) are not good enough. Although catalysis may yield a pyrolysis liquid with less increase in viscosity upon standing, no clear oxygen reduction or defunctionalization is noted.[22] Similarly, impregnation of the biomass with potassium or magnesium salts can reduce the decomposition temperature of the biomass, but does not reduce the oxygen content or its acidity.[23] On the contrary, magnesium promotes dehydration reactions, leading to a more viscous product.

On an overall process level, the typical carbon yields at high severity are close to the original lignin content of the wood. It can be suggested and justified that catalytic pyrolysis appears to favor the production of deoxygenated products from the lignin fraction only, whereas the carbohydrates are converted to coke, gas, and water. This hypothesis requires further proof, as there are also indications that aromatics can be produced from cellulose.[24] Experiments might be done by taking the pyrolysis lignin separated from the pyrolysis liquid as a feed material to show elevated yields of aromatics. Figures 3 and 4 show that carbon yields of near 50 wt % (corresponding to the 92 gallons per BDT referred to by KiOR) are unrealistic and far too optimistic on basis of the literature data provided here. Carbon yields at complete deoxygenation levels will probably be lower than 20 wt %, values close to the 30 gallons per BDT published in 2014. Although no detailed information is provided by two other companies claiming that they will commercialize catalytic fast pyrolysis within the next few years, Annelotech and BioBTX, it seems likely that these figures will be realistic. In the ex-bed option, the temperatures of the fast pyrolysis and the further catalytic deoxygenation of the vapors can be individually controlled, but the results shown in Figures 3 and 4 for these options are remarkably similar.

Assuming the low carbon yields to liquids, well below 20 wt %, ‘severe’ catalytic pyrolysis of biomass to liquid fuels is probably barely economically feasible. It might be reasonable only if the focus is redirected towards high-value-added chemicals (of which BTX might be an example, but also the olefins will have a certain value if they can be properly handled at the pyrolysis site) or when the conversion of the initially more stable lignitic fraction is aimed at.

A better option is the more controllable way to catalytically deoxygenate (or to defunctionalize) such liquids at temperatures at which the thermal pathways are mostly absent. So far, hydrotreatment of the liquids, or an integrated approach suggested by GTI (the so-called integrated hydropyrolysis and hydroconversion (IH2) seem better alternatives. The latter (IH2) includes the in-bed catalysts and hydrogen in a high pressure fast pyrolysis process, combined with ex-bed hydrotreating over hydrogenation catalysts. Figure 9 presents an overview of yields and deoxygenation rates for these processes:

- Fast pyrolysis followed by a hydrotreatment (carbon yields on the order of 35–45 wt % at 100 % deoxygenation rates)[25]
- The IH2 process yielding values between 43 and 47 wt % for wood and seaweed,[26]
- KiOR, reporting 30 gallons per dry ton biomass (near 17 wt % carbon yield).

Figure 9. Comparison of yields for fast pyrolysis, catalytic pyrolysis, conventional fast pyrolysis followed by hydrotreatment, KiOR’s published yield, and yields reported for the IH2 process.
Finally, in literature quite some efforts have been devoted to detailed analysis of pyrolysis liquids; usually, not as well as catalytic. It can be stated that the chemical products should be analyzed up to the full extent possible in an effort to move beyond existing insights. Some of these analysis tools may be useful but sometimes too complex for the current state of development. As a recommendation, and to allow a much better comparison of data from literature, it is suggested that at least the following, rather straightforward, analysis on the liquids is provided:

- Elemental analysis (at least carbon, hydrogen, and oxygen) of feed and all products obtained from catalytic pyrolysis and a clear representation of yields and elemental composition in terms of as received or dry ash free. One simple option is to dewater the liquids before further analysis (for example by vacuum distillation, allowing a minor error in the overall carbon balance due to the loss of small organic components); preferably a complete elemental balance for the complete product slate is provided.
- Gel permeation chromatography (GPC) analysis to provide information on the molecular weight distribution of the oils: Complete GPC plots are relevant as only weight or number-averaged molecular weights do not provide sufficient information on the sample. In addition, care should be taken in the actual analysis method while using liquids derived from the fast pyrolysis of biomass.[27]
- Data on the charring behavior of the liquid product; a representative parameter in this area is the micro-carbon residue test unit, a standardized and easy tool to evaluate the charring tendency by micro carbon residue testing (MCRT) or by thermogravimetric analysis (TGA).

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The pitfalls of pyrolysis: Catalytic pyrolysis is seen as a promising route to yield liquids with a higher quality. However, in an initial stage of the catalytic process, reactive components are mainly converted to coke, gas, and water, and to a limited extent to a liquid product. Catalysts are not good enough, and finding ones to yield improved quality liquids may be practically impossible.