DOI: 10.1002/anie.201007508

# Production of High-Quality Diesel from Biomass Waste Products**

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Biodiesel, or FAME (fatty acid methyl ester), has been promoted for the last decade as substitute for fossil-based diesel. However, it soon became evident that its production competes with food production by engrossing agricultural crop land. A similar issue occurs with bioethanol if this is produced by fermentation of edible sugars. Therefore, energy roadmaps have been revised and the production of a second generation biodiesel from carbohydrate-derived biomass has been proposed. The carbohydrates occur predominantly in nature in the form of biopolymers, such as cellulose, hemicellulose, and lignocellulose. The hexose and pentose building units are highly oxygen-functionalized and have to be dehydrated and hydrogenated and several molecules have to be condensed to obtain hydrocarbons with ten to eighteen carbon atoms within the diesel fraction (Scheme 1).

$$n\,C_6H_{12}O_6 + m\,H_2 \longrightarrow H-(CH_2)_k-H \; + l\,H_2O$$

***Scheme 1.*** The formation of diesel fuel from monomeric hexose sugar molecules. Ideally, *k* is in the range of 10 to 18 and consequently *n* is 2 to 3.

It is obvious that Scheme 1 describes a challenge rather than a specific solution, thus leaving room for the interpretation and creativity of chemists and engineers. Several routes are being developed to convert biomass into drop-in replacements for diesel fuels.[1,2] One possibility is to break down the biomass into carbon monoxide and hydrogen to produce syngas that can be transformed into waxes by the Fischer–Tropsch synthesis (FTS). In this process, gasoline or diesel fuel cannot be made selectively in a direct manner and the waxy FTS product has to be converted into premium diesel in a hydrocracking unit.[3]

In another more simple approach, fast pyrolysis (FP) or catalytic fast pyrolysis produces a liquid that is called bio-oil. With the FP process, apart from the large amounts of char produced, the resulting bio-oils contain, among others, important amounts of alcohols, aldehydes, ketones, acids, and aromatics that have to be further upgraded to produce gasoline-range aromatics.[4] Alternatively, cellulosic biomass can be hydrolyzed under mild conditions into its monomers, producing sugar molecules. These molecules can be fermented with genetically altered microorganisms into hydrocarbons,[5] or dehydrated chemically into 5-hydroxymethylfurfural (HMF) or into furfural (FUR) when starting from hexoses or pentoses, respectively. Reacting these intermediates further, liquid alkanes ranging from $C_7$ to $C_{15}$ can be produced by aqueous phase processing.[6,7] In this case, the connection between different molecules to meet the number of carbon atoms for the aimed fuel range is achieved by an aldol condensation reaction in presence of a basic catalyst and with acetone as a second reactant.

A very recent approach to produce kerosene has been introduced with $\gamma$-valerolactone, which is obtained from biomass-derived carbohydrates via levulinic acid.[8] The latter undergoes decarboxylation at 375 °C and 36 bar over a silica/alumina catalyst to produce butene and $CO_2$, being the former oligomerized to octenes and hexadecenes in a second step.

This list of processes to produce second-generation biofuels can be further expanded,[9] but the extent to which one of these technologies will play an active role in the future biofuel industry will depend on economics, energy efficiency, and environmental issues.[3] Surplus energy consumption and process limitations can be detected in most of the processes proposed to date. For example, the excessive cleavage of carbon–carbon bonds and subsequent reformation leads to energy losses. Extractions of products with organic solvents are energy and cost-intensive steps that change, to the worse, the overall energy balance of the process. Organic solvents as reaction medium should be avoided, as they enlarge process volumes with a negative impact on process economics and environment. A crucial point for the optimization of the overall process economics is the perfect overlap of the boiling point range of the product mixture, with diesel range $C_9$ to $C_{24}$ hydrocarbons.

By considering all of the above described limitations, we have designed a sustainable process, based on reactions other than those reported before, which involves hydrophobic intermediates and produces nonpolar alkane products suitable for high-quality diesel fuel. This strategy implies that, owing to the polarity of the products, water separation by distillation is not required, but an automatic, energy-neutral physical separation of (intermediate) products from water will occur reducing energy consumption in the process.

We propose second-generation biocarburants and a process to produce them starting from 2-methylfuran (2MF). The precursor of 2MF, namely furfural (FUR), is available on an industrial scale.[10] Indeed, batch and continuous processes have been run for decades to produce FUR in

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[**] This work was supported by Consilider Ingenio 2009 CDS 00050. O.d.l.T. is grateful to the Spanish Ministry of Science and Innovation for a doctoral grant (FPU). We also thank E. Ponce and Dr. D. Penno for discussions and technical assistance.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201007508.

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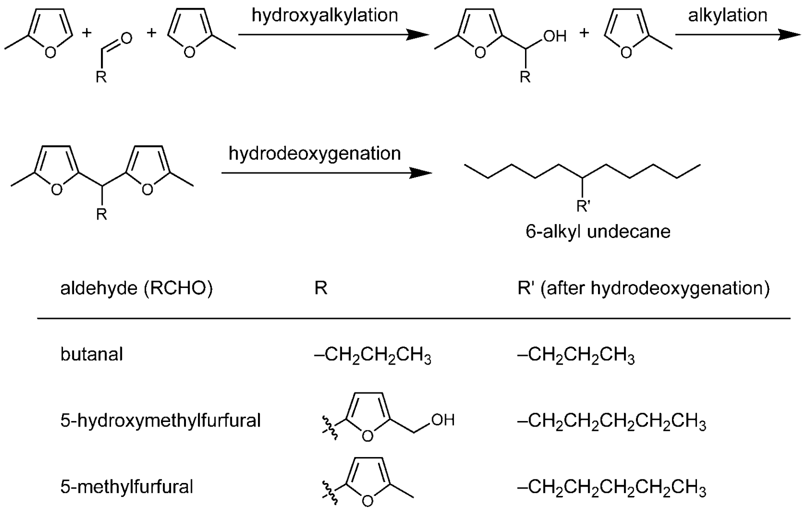
$280 \times 10^3$ tones per year directly from non-edible biomass, such as corncobs, oat hulls, almond husks, bagasse, sunflower husks, residues of olive extraction, and many other biomasses that are rich in pentose biopolymers.[11] 2MF is obtained from FUR in the industrial production of furfuryl alcohol,[12] and its concentration in the effluent can be increased up to 93% selectivity simply by raising the reaction temperature from 135 °C (for production of furfuryl alcohol) to 250 °C.[12,13]

There are important advantages in using 2MF as a starting material owing to its hydrophobic nature that allows separation from water at room temperature and the high reactivity and selectivity for alkylation reactions.[14] Thus, we thought of producing long chain alkanes within the kerosene-diesel range by means of cascade hydroalkylation/alkylation reactions of 2MF. The starting hypothesis is that with 2MF, selective hydroalkylations could be carried out, and polymer formation should be inhibited since one of the two reactive α-positions is "protected" by the unreactive methyl group. These hydroalkylations/alkylations can be performed in presence of soluble or solid acids,[15,16] and when selective, the only by-product is water.

The validity of the concept was shown by reacting 2MF with butanal as a test reaction, and from the successful results, we show the direct trimerization of 2MF (no any other reactant added). During the test reaction it was found that with acid catalysts bisylvylalkane molecules with fourteen carbon atoms are formed but no polymeric structures with more than two furan moieties. Then hydrodeoxygenation of the bisylvylalkanes give linear alkanes with branching in the middle of the chain (for example, an isomer of tetradecane; see Scheme 2). More specifically, and after hydrodeoxygenation of the intermediate bisylvylalkanes, product mixtures were obtained in excellent yield that can be used for direct blending for high-quality diesel.

Alkylation and hydroalkylation of 2MF can be performed using liquid or solid acids. Here we worked under solvent-free conditions using either *para*-toluenesulfonic acid (*p*-TosOH) or the Amberlyst 15 resin, as soluble and solid acid catalyst respectively, for performing the hydroalkylation/alkylation of 2MF with butanal. With 2.5 wt% of *p*-TosOH and a 2:1 molar ratio (stoichiometric ratio) of 2MF and butanal, 85% conversion with 91% selectivity was obtained (Supporting Information, Table S1, entry 1). The values can be increased to 93% conversion and 95% selectivity by working with a small excess of 2MF (Supporting Information, Table S1, entries 2 and 3). The procedure is very simple, and the crude reaction mixture separates rapidly into two phases upon standing. The lower aqueous phase containing the acid catalyst (when soluble) was separated (see Supporting Information). We have seen that under the same reaction conditions it is also possible to use a solid catalyst in the hydroxyalkylation/alkylation of 2MF, and the results are given in the Supporting Information, Table S1.

The second step in the process, that is, the hydrodeoxygenation of the 1,1-bisylvylalkanes (1,1-bisylvylbutane) was performed in a fixed-bed continuous reactor directly as a neat liquid without solvent. Results in Figure 1 and the Supporting Information, Table S2 show nonane, 4-propylnonane, 6-propylundecane, and $C_{14}H_{28}$ monocyclic alkanes as predominant alkane products. Good results were obtained with platinum on carbon and alumina. The carbon balance was 98%, being almost 90% in the liquid organic phase; the rest of the carbon-containing products were $C_4H_{10}$, $CH_4$, CO, and $CO_2$, with very small amounts of $C_2/C_3$ (Supporting Information, Figure S1). In the liquid organic phase, approximately 95% of the products are alkanes, with 76%, 17% and 2% of $C_{14}$, $C_9$, and $C_{12}$, respectively. Although there is no doubt that the process could be optimized to produce even a higher yield of liquid alkanes, the results obtained herein are already a significant benchmark. We have run the process in the laboratory for more than 140 h with constant activity and selectivity (Supporting Information, Figure S2), and the future perspectives of the process are even more promising if one considers the excellent pour point (−90 °C) and cetane number (70.9) of the total organic fraction obtained. Therefore, blending conventional carburants with the new second-generation biocarburant based on 6-alkylundecanes will improve cetane number and their flow properties at low temperature.



***Scheme 2.*** Formation of 1,1-bisylvylalkanes by hydroxyalkylation/alkylation from Sylvan and an aldehyde with subsequent hydrodeoxygenation to 6-alkyl undecane.

After the successful results obtained with the test reaction, the synthesis of diesel was attempted starting only from 2MF, that is, no any other reactant added, by generating in situ 4-oxopentanal from 2MF (Scheme 3). The 4-oxopentanal will react with two other molecules of 2MF, and the hydrodeoxygenation of the intermediate should give pentadecane isomers as the main products.

Water is added to 2MF under acidic conditions and furan ring-opening occurs, giving 4-oxopentanal. The hydroxyalkylation/alkylation reaction of 2MF with 4-oxopentanal is so fast that the aldehyde can hardly be detected in the reaction mixture. It appears that this trimerization reaction of 2MF is a very sustainable reaction, as no by-products are obtained (see Scheme 3). The trimeriza-

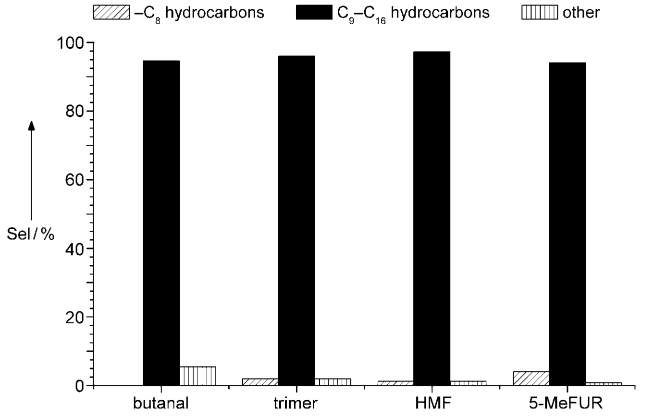
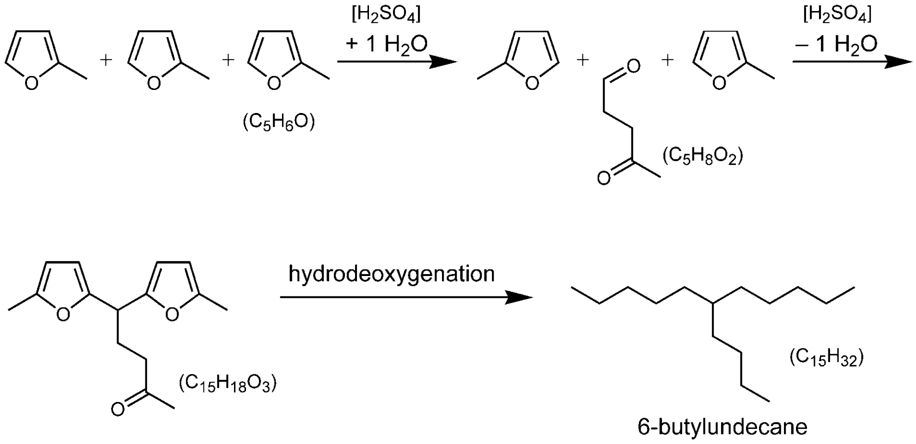


***Figure 1.*** Product selectivities (Sel) for the liquid organic phase produced in the hydrodeoxygenation of the corresponding bisylvyl precursors synthesized from Sylvan and either butanal, 5-hydroxymethylfurfural (HMF), 5-methylfurfural (5MeFUR), or of the Sylvan trimer. Conversion was complete in all cases and the liquid organic phase adds to 85–96.5 % of the employed carbon atoms.



***Scheme 3.*** Formation and hydrodeoxygenation of 5,5-bisylvyl-2-pentanone. Initially, one molecule of Sylvan is hydrolyzed to 4-oxopentanal by sulfuric acid catalysis; two further Sylvan molecules are subsequently hydroxyalkylated and alkylated with the intermediary aldehyde. Overall yield from Sylvan to diesel: up to 87%.

tion has been optimized using sulfuric acid as catalyst, and 94 % of a crude reaction mixture containing 76 % 5,5-bisylvyl-2-pentanone was obtained (Scheme 3). As reported before, the aqueous phase, containing the soluble acid catalyst, separates on standing from the organic product and could be physically separated and re-used. We have recycled the acid solution ten times without observing any loss of activity or selectivity. Although sulfuric acid cannot be considered a sustainable catalyst, it should be taken into account that it is recovered and recycled several times. Nevertheless, preliminary results indicate that environmentally friendly solid catalysts can also be used.

If the $C_{15}$ diesel precursor 5,5-bisylvyl-2-pentanone was distilled and submitted to the hydrodeoxygenation (ratio of the amount of catalyst [g] to feed rate [g min$^{-1}$], W/F 43 min), a similarly high amount of diesel as before was obtained in the liquid organic fraction (Figure 1). However, for practical use, distillation of the $C_{15}$ precursor is not necessary and the crude from the trimerization of 2MF (94 % yield) can be directly fed to the hydrodeoxygenation reactor. Then the diesel selectivity in the hydrotreated liquid organic phase was 96 %. The final result after the two-step process gives an overall yield of diesel of 87 %, which is the best yield reported to date. The gaseous by-products ($C_1$ to $C_4$: 2 %) and the low-weight hydrocarbons ($C_4$ to $C_8$: 2 %) can be employed for heat generation, so water remains the only resultant by-product (Supporting Information, Figure S3).

The process described herein opens new routes for producing high quality diesel from waste biomass. Indeed, we can envisage two other processes that we are currently working out in which 5-hydroxymethylfurfural (HMF) and 5-methylfurfural derived from hexoses are reacted with 2MF in the presence of an acid catalyst under similar conditions as employed before for butanal and 2MF (see Scheme 2 and the Supporting Information). First results indicate that the corresponding bisylvyl intermediates are obtained in 86 % and 93 % yield, respectively. After hydrodeoxygenation, 95 % of the liquid organic phase was suitable for the diesel fraction (Figure 1).

In conclusion, we have presented a simple process for converting 2-methylfuran (Sylvan), which can be obtained from biomass wastes, such as corncobs, oat hulls, bagasse, and sunflower husks, into high-quality diesel fuel through two consecutive catalytic steps that involve hydroxyalkylation/alkylation and hydrodeoxygenation, with an overall yield of 87 %. The process is easy to carry out, is energy efficient, and does not involve organic solvents. It has been demonstrated that the first step, namely the hydroxyalkylation/alkylation reaction of 2MF, can be carried out conveniently with a broad variety of aldehydes, for example with 5-hydroxymethylfurfural and 5-methylfurfural obtained by hexose dehydration. The process is very stable at laboratory levels (more than 140 h) and produces diesel-range products with excellent pour point and cetane number that are suitable for direct blending with conventional diesel.

## *Experimental Section*

Trimerization of 2-methylfuran: In a typical experiment, 2-methylfuran (Sylvan, 328 g, 4.00 mol), sulfuric acid (98 %, 78.7 g, 0.802 mol, 24 wt %) and water (249 g, 76 wt %) were heated to 60 °C and stirred for 16 h. The aqueous phase was separated and kept for further reactions (96 % of the initial amount recovered). The organic phase was treated with $NaHCO_3$ and $MgSO_4$ and then filtered. A brownish liquid was obtained with a 79–80 % content (GC) of 5,5-bis(5-methyl-2-furanyl)-2-pentanone (308 g, 1.25 mol, 94 % yield).

Hydrodeoxygenation: The catalyst (8 g; 6.8 g of 3 wt % Pt on active carbon and 1.2 g of 3 wt % Pt on $TiO_2$ as a physical mixture) was placed in the stainless steel tubular reactor and activated (hydrogen flow of 450 mL min$^{-1}$ at 400 °C and 5 MPa hydrogen pressure, 1 h). The trimerization crude reaction mixture (275 g) was passed down-flow with a rate of 0.12 mL min$^{-1}$ with the same hydrogen flow and pressure as during the activation step and was mixed with the hydrogen flow before entering the reactor. The reaction temperature was 120 °C at the entry of the reactor with a gradient to the middle of the reactor and 350 °C in the second half of the reactor. Two liquid phases were obtained with a total weight of 286 g, being the aqueous phase 20 % of the total amount. The liquid organic phase (yield 96.5 %) was analyzed on an Agilent gas chromatograph equipped with a flow modulator; 96 % were classified as $C_9$ to $C_{16}$ hydrocarbons (linear, branched, monocyclic, and bicyclic; less than 3 % aromatic), less than 2 % as low-weight hydrocarbons ($C_3$ to $C_8$), and less than 1 % were oxygenated compounds. In the gaseous effluents less than 2 % of the employed carbon was detected.

Received: November 30, 2010

Published online: January 31, 2011

**Keywords:** biomass · diesel fuel · lignocellulose · sustainable chemistry

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