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Production of Biofuels – The Hydrogen Consumption as Performance Indicator in the Early Design Stage

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Abstract

Lately, biomass is more and more considered as a raw material in the processing of chemicals and fuels, but only few production processes are established until now. Instead, a lot of individual reaction alternatives are explored and very little information is available to predict their potential in integrated biorefinery concepts. In this contribution feasible production strategies for biofuels are systematically identified and subsequently analyzed applying Reaction Network Flux Analysis (RNFA) [1]. In the analysis, the hydrogen consumption is chosen as performance indicator to compare different scenarios. Based on the results, a classification of solutions is possible such that promising reaction pathways as well as bottlenecks can be detected. Thus, RFNA is an efficient tool to deal with complexity of the early design stage and to obtain first important information in terms of conceptual process development.

Keywords: *biorefinery, biofuels, Reaction Network Flux Analysis, hydrogen*

1 Motivation

Due to the limited availability of fossil resources, an increasing energy demand and rising carbon dioxide emissions, renewable raw materials are attaining a special interest in the transportation fuel sector. Whereas most approaches focus on the production of biodiesel or bioethanol, it is also possible to develop synthetic biofuels. Here components and blends with excellent fuel properties can be chosen, which can be efficiently produced from biomass feedstock. However, converting the oxygenated biomass into suitable fuels by removing oxygen in form of water requires large amounts of hydrogen. Therefore a sustainable hydrogen supply is of utmost importance. To meet this demand, research activities are run in the field of electrolysis (with sustainable electricity sources like solar or wind energy), photo- or thermophilic fermentation and steam reforming or pyrolysis of biomass. Especially, if biomass is considered as feedstock for both, hydrogen and fuel production, integrated biorefinery concepts must be evaluated in the early design phase. The problem complicates as only few (bio-)catalytic routes for the conversion of biomass are established, which in turn provides the opportunity for exploration and innovation. So the hydrogen need (among others) can be utilized as an evaluation criteria for the selection of synthesis routes. In this contribution we show how Reaction Network Flux Analysis (RNFA) can be applied to analyze integrated biorefinery concepts for the production of biofuels.

2 Approach

In the cluster of excellence “Tailor-made Fuels from Biomass” an interdisciplinary research approach is followed to develop sustainable production processes for synthetic biofuels [2]. By defining the optimal combination of fuel blend and low-temperature combustion engine, the engine efficiency should be improved while the emission ratio is reduced. Besides novel chemical synthesis routes are explored such that the functional structure of biomass is preserved. From the beginning, experimental work on reactions and catalysts should be accompanied by conceptual design to classify the large number of alternative production pathways according to the data at hand. For this purpose, Reaction Network Flux Analysis (RNFA) is applied [1].

This systematic approach for material flow analysis is derived from metabolic pathway analysis [3]. For the analysis of the different reaction pathways, all possible reactions are summarized in a network, where substances and reactions are represented by nodes and arcs respectively. Mole balances are performed for each node taking the stoichiometric coefficients into account. As a substance can generally be formed by one or more reactions, the corresponding system of equations is underdetermined such that room for mathematical optimization is given. If the yield of the target component b_{target} is supposed to be maximized, the linear optimization problem

$$\begin{aligned}&\max_{x,b} b_{\text{target}}\\ &s.t.\quad Ax = b\\ &\qquad x_j \le \eta_j \sum_{k,k\neq j} \nu_k x_k \quad \forall j\\ &\qquad x,b \ge 0\ ,\end{aligned} \tag{1}$$

can be formulated where A is the matrix of stoichiometric coefficients. The molar flux through the network is x, while b balances the product and by-product formation at each node. In addition yield constraints are introduced to limit the conversion of certain reactions. Here, η refers to the molar yield of a reaction j and k is the set of fluxes entering or leaving the associated node.

The solution of the optimization problem identifies the best reaction pathway according to the chosen objective function, whereas a reaction pathway consists of the active reaction steps between starting and target molecule. For a comprehensive analysis it is necessary not only to know one, but all reaction possibilities. These can be detected by adequate mixed-integer programming techniques [4]. Once the flux scenarios are identified, they can be classified according to different criteria, which are either directly linked to the mass balance or expanded by economic, energetic or ecological aspects. Based on this knowledge bottlenecks as well as most promising reaction pathways can be detected and further research activities can be guided properly.

On the one hand the reusability of the network enables the fast calculation of case studies varying i.e. the biomass composition, reaction yields or the objective function. On the other hand promising solutions are pointed out by the successive analysis and can be refined by adding criteria of conceptual process design like separation index or energy demands. The combination of these two aspects offers the basis for a rapid evaluation of alternatives in the early design stage.

3 Application to Biofuels

RNFA is now applied to evaluate the production of different biofuels in integrated biorefinery concepts focusing on the hydrogen provision. Therefore a network covering reactions from biomass towards fuel components is constructed. Based on the literature [5, 6, 7], admissible reactions increasing the hydrogen to carbon ratio and decreasing the oxygen to carbon ratio at the same time are selected for the network, which finally consists of 125 reactions and 87 substances. For most reactions no yield predictions can be found in literature, such that a yield of 97% is assumed for these reactions accounting for unavoidable losses.

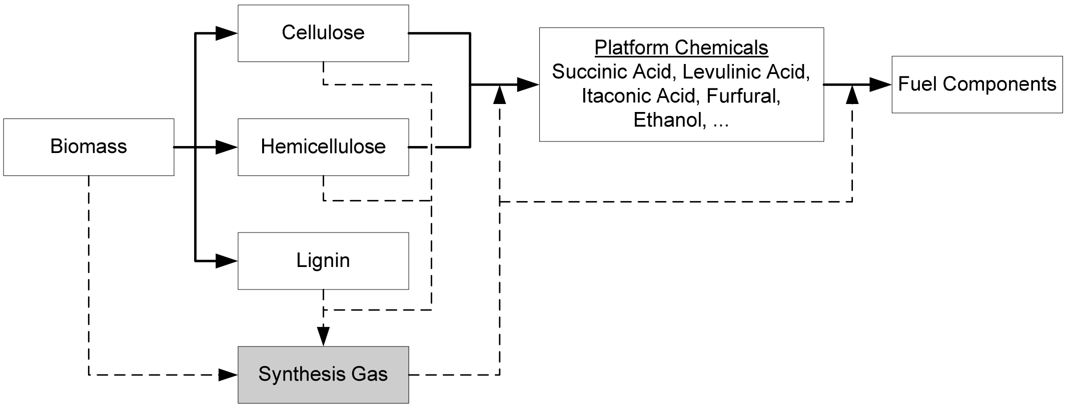

Figure 1: Processing scheme of biomass.

Figure 1 shows the underlying structure of the reaction network. In a first step biomass is decomposed into its main components cellulose, hemicellulose and lignin. While cellulose and hemicellulose can be transformed into platform chemicals, lignin can only be converted into synthesis gas. Further reactions describe the formation of synthesis gas using biomass, cellulose or hemicellulose. Instead of defining a particular processing technique for the production of synthesis gas, ideal conditions are assumed for gasification and subsequent purification. Synthesis gas itself can be returned to the network as hydrogen source or as a feedstock for the production of additional reactants like methanol such that biomass is the only feed to the network.

As the criteria for the selection of a suitable biofuel is still an open research problem, the energy of combustion is chosen as representative fuel property in this case study. Unfortunately, experimental values for the energy of combustion are not available for all substances such that they have to be calculated based on Joback's group contribution method [8]. According to this data, the five network components with the highest combustion energy are selected as target molecules.

For each target molecule the ten best reaction pathways are identified by solving the optimization problem (1). To account for changes in the biomass feedstock, two different scenarios are investigated. In the first scenario biomass has a high cellulose and a low lignin fraction (cellulose 75%, hemicellulose 15%, lignin 10%), while in the second scenario biomass with a low cellulose and a high lignin fraction (cellulose 40%, hemicellulose 35%, lignin 25%) is supplied. Lower and upper bounds on the individual fractions are set according to data provided by Huber et al. [5].

4 Results

The case verifies the assumption that the hydrogen need for the production of biofuels can be fairly high. Depending on the target molecule and on the production route, up to 6.5 mole hydrogen are required per mole product. Still, the hydrogen supply for direct use or for the production of additional reactants is not the limiting factor in any of the reaction pathways. In fact, the actual yield in the reaction steps from biomass to platform chemicals is so low that a sufficient amount of hydrogen can always be provided by the gasification of the residuals.

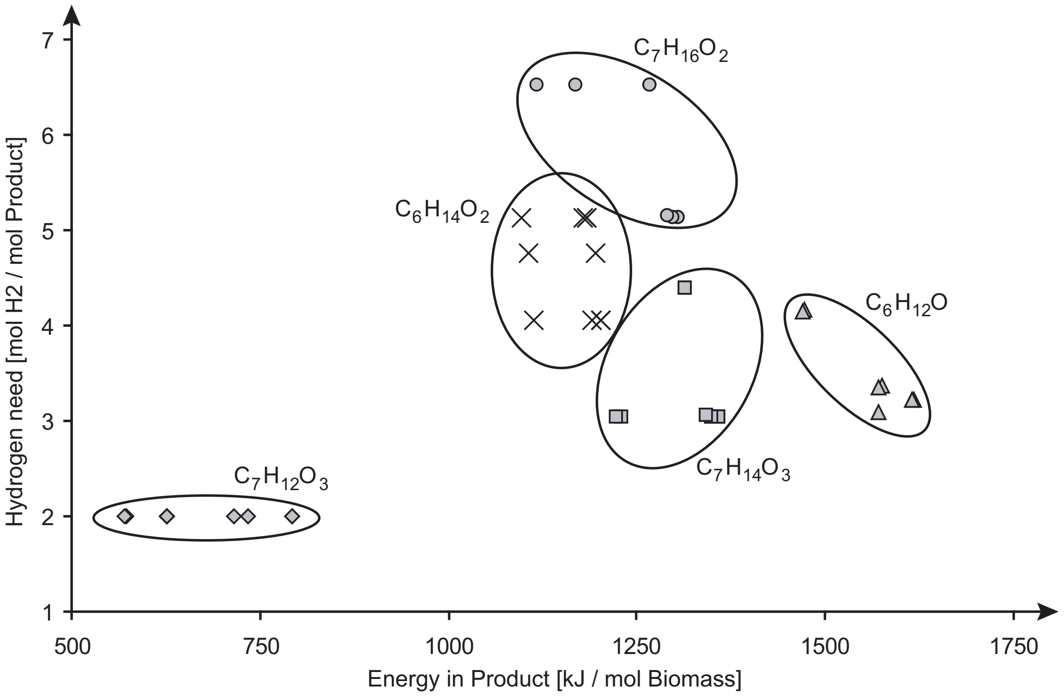

Figure 2: Comparison of production pathways for different biofuels (different symbols) starting from biomass with high cellulose content.

However, the production alternatives strongly vary in their hydrogen consumption such that it is a good performance indicator in terms of sustainable raw material utilization. Residuals can be recycled elsewhere (i.e. to meet the energy demand), if they are not needed in the hydrogen chain. Figure 2 shows the results for scenario one, where a feedstock with a high cellulose fraction is supplied to the network. For the different production routes of a target molecule, the hydrogen need is plotted against the amount of combustion energy, which can be obtained per mole of biomass. It can be seen that the reaction pathways are spread over a wide range, but obviously pathways with good energy efficiencies and low hydrogen demands are desired.

All target components have a similar molar energy of combustion, but the product yields of $C_7H_{12}O_3$ (3-(hydroxymethyl)-, ethyl ester-3-butenoic acid) are so small that it is not competitive with the other molecules. In this case great amounts of by-products are formed.

In contrast $C_6H_{12}O$ (dimethyltetrahydrofuran, DMTHF) outperforms the other substances in terms of energy at comparable hydrogen needs. Moreover, significant differences also exist between the alternative pathways producing the same target molecule. Especially, for $C_7H_{16}O_2$, $C_6H_{14}O_2$ and $C_7H_{14}O_3$ (1,4-dimethoxy-2-methyl-butane, 1,4-dimethoxy-butane, 4-methoxy-3-methyl-, methyl ester- butanoic acid) one can find solutions, which offer either a higher energy level at the same hydrogen demand or a lower hydrogen demand at the same energy level. Both examples show that target molecules cannot only be selected based on their combustion properties, but that their production routes must directly be taken into consideration.

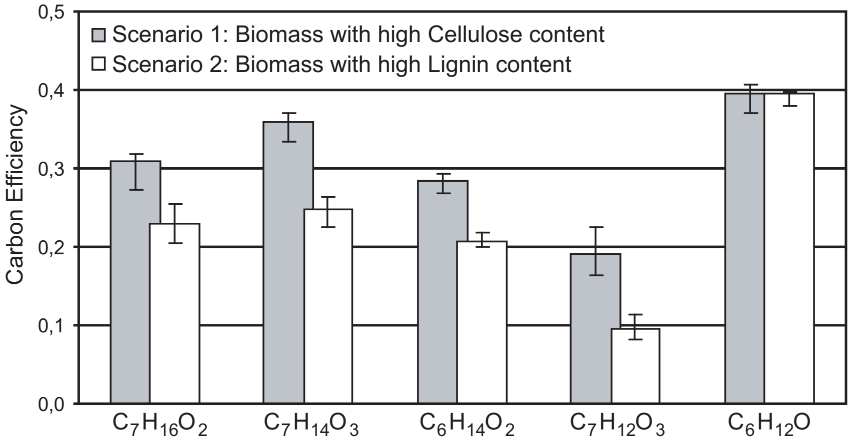

Figure 3: Carbon efficiency of selected target molecules for two feedstock scenarios. The “error bar” refers to variations in the production routes linking feedstock and target molecule.

For a further analysis of the two biomass scenarios, carbon efficiency is selected as a performance indicator, which relates the amount of carbon in the product to the one in the biomass feedstock. With a value below 40%, the carbon efficiency is very low for all the molecules. This is again due to the limited conversion in the reaction steps from biomass to platform chemicals.

In Figure 3 the mean values of the carbon efficiency are compared for both scenarios. The deviation from the average indicates the best and the worst production route. In most cases the carbon efficiency decreases, if the processed biomass has an elevated lignin fraction. The pathways are sensitive to these changes in the feedstock because lignin cannot directly be converted into functional compounds. DMTHF proves an exception to this rule. The average as well as the optimal values of the carbon efficiency remain largely unaffected, even though the composition of the feedstock changes. This can be explained by the fact that DMTHF can be produced on the basis cellulose and hemicellulose and the collective fraction of the two is not strongly affected by changes in the feedstock. Thus, if major changes in the feedstock are expected, this must be considered in the selection of target components and production routes.

As a result of this analysis, the component DMTHF is identified as most promising fuel candidate. It can be produced efficiently with a low hydrogen need and the reaction pathway is not sensitive to changes in the feedstock composition.

5 Discussion and Conclusions

Even though the hydrogen demand can be covered by gasification of residuals, the carbon efficiency is very low in all cases. Consequently, future research must focus on increasing the carbon efficiency. On the one hand the conversion from biomass to platform chemicals must be improved, on the other hand efficient processing techniques for lignin must be developed such that lignin can directly be transformed into chemicals while the hydrogen need is met by other sustainable resources.

The study clearly shows that crucial information can be deduced from RNFA. It allows a systematic analysis of reaction pathways in order to evaluate production routes for promising fuel candidates. While hydrogen consumption and carbon efficiency have been used in this study, many other (alternative or additional) performance indicators can be accommodated in a straightforward manner.

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