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Conversion of Waste Biomass into Second-Generation Biofuels in School Chemistry Education

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Abstract

The steadily increasing consumption of limited fossil resources and the increasing threat of a progressing climate change direct more attention towards renewable energy sources. Despite the research activities in this field, a sustainable energy supply currently remains a rather long-term goal and many technical challenges still need to be overcome. One of the main problems of technologies such as solar and wind power is their unreliability and, more precisely, the lack of technical capabilities to store excess amounts of producible electric energy [1].

Until more advanced and affordable technologies and solutions to these problems become widely accessible, power-to-liquid-systems represent an interesting solution, which additionally incorporates the idea of sustainability. These systems enable the storage of excess energy from renewable energy sources, e.g. the synthesis of conventional energy carriers out of biomass. This pathway has gained more attention recently, since a new method was presented describing the synthesis of octane via an easy Green Chemistry electrolysis out of levulinic acid [2]. In this contribution, a course design will be presented, reflecting the power-to-liquid-concept on the example of the conversion from waste biomass to octane. Within several (model) experiments, every step of this process can be illustrated in school chemistry education using common chemicals and equipment, leading from the synthesis of levulinic acid out of cellulose up to the electrochemical synthesis of octane.

1. Introduction

Exhaust gases, greenhouse effects, pollutants – conventional fuels such as gasoline and diesel are often associated with climate change and impending consequences for our environment. Not without good reason, since road traffic causes almost a quarter of the global CO_2 emission. Despite the apparent political effort to implement new concepts of (electric) mobility, combustion engines and thus the production of conventional fuels will continue to play a major role for decades, particularly in emerging and developing countries. Special opportunities in terms of sustainability are offered in combination with other renewable energy sources (hydropower, solar, wind). Instead of storing the overcapacities occurring during peak periods in expensive electricity storages, they can also be used for the synthesis of fuels. The existing infrastructure can then be used for storage, transport and logistics.

For these reasons, new and sustainable synthesis concepts for conventional fuels are not only a current and important topic in research and industry, but also offer various learning opportunities for school chemistry education. While several experiments, such as the synthesis of biodiesel or bioethanol out of vegetable oil or crop, have already been described for chemistry class [3,4], the use of edible biomass or cultivable land for the production of fuel remains ethically questionable ("Fuel vs. Food" debate) and has been controversially discussed in the media [5]. As a consequence, so-called second generation biofuels are recently gaining a lot of interest as they are exclusively produced out of organic waste and thus do not compete with food production.

In this contribution, a course design will be presented focusing on the conversion of waste biomass into sustainable, second generation biofuels. Starting with the extraction of cellulose, the laboratory course further describes an easy method to gain levulinic acid, which is subsequently electrochemically converted into valeric acid and later into octane. Within this course design, several typical contents of the high school chemistry curricula such as electrolysis, alkanes, redox reactions and fermentation can be either introduced or deepened. Furthermore, the course topic offers several points of reference linking these concepts to students' everyday lives. Finally, since two of the main challenges of the 21st century are said to be the supply and consumption of energy, the students'

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consequent findings serve as the basis for discussions regarding the explored and further related topics.

2. Students' Perspectives on the Conversion of Biomass

Students' perspectives play a key role regarding their learning success [6]. While their perspectives on the production of energy from main renewable sources are widely known [7,8], no detailed focus has yet been placed on the conversion of biomass. The present study thus focuses on the acquisition of (1) students' subject matter related scientific knowledge, (2) their ability of evaluating the effects of biomass conversion, (3) their opinion and (4) interest in the topic. For this purpose, a questionnaire (paper-pencil-test) for the target group (students aged 15 – 18, N = 68) was designed. Figure 1 shows selected results.

	Results / Conclusions	Students' Statements
Subject-related knowledge	• prior knowledge is widely varying • students name many possibilities of usage • knowledge yet remains often superficial • general misconceptions (*e.g.* biomass sources, biofuel sustainability, CO_2 footprint)	*"energy and gas production" / "fertilizers, biofuels"* *"rapeseed oil → fuel"* *"biofuels have lower CO_2 emission than oil-based fuels"*
Socio-economic assessment	• environmental friendliness of biofuels are highlighted (65 %) • "Food vs. Fuel" Discussion named as a point of criticism (26 %) • assessment mostly limited on first generation biofuels	*"environmentally friendly and sustainable"* *"cultivable land should not be used for rapeseed instead of food"* *"moral conflict: should arable land be chosen for energetic use while there are famines elsewhere?"*
Personal opinion	• majority opting in favor of further support of this technology (75 %) • main reasons: sustainability, protection of the environment	*"in my opinion, it has positive consequences for the environment, since there will be less CO_2 emissions when E10 biofuel is used"*
Interest in topic?	58 % stated high or very high interest in an implementation into school chemistry	

Figure 1: Selected perspectives and statements of students.

From these results, three implications for teaching can thus be derived:

- The existing knowledge about the properties and possible uses of biomass has to be addressed and deepened, in particular with regard to the extraction of biofuels.
- Students associate the term biomass mainly with agricultural crops such as rapeseed or corn - this concept should be extended by other aspects such as plant waste.
- Second generation biofuels should be addressed as an ethically justifiable variant and evaluated from a societal, environmental and economic perspective.

3. Course Design

Based on the obtained students' perspectives, several teaching materials and experiments on the conversion of biomass for school chemistry education have been developed. Figure 2 provides an overview of some possible contents and links. Given the extent of that field and the limited classroom time, the listed modules can thus be used individually for the development of teaching units, depending on the teacher's objectives or the students' interests.

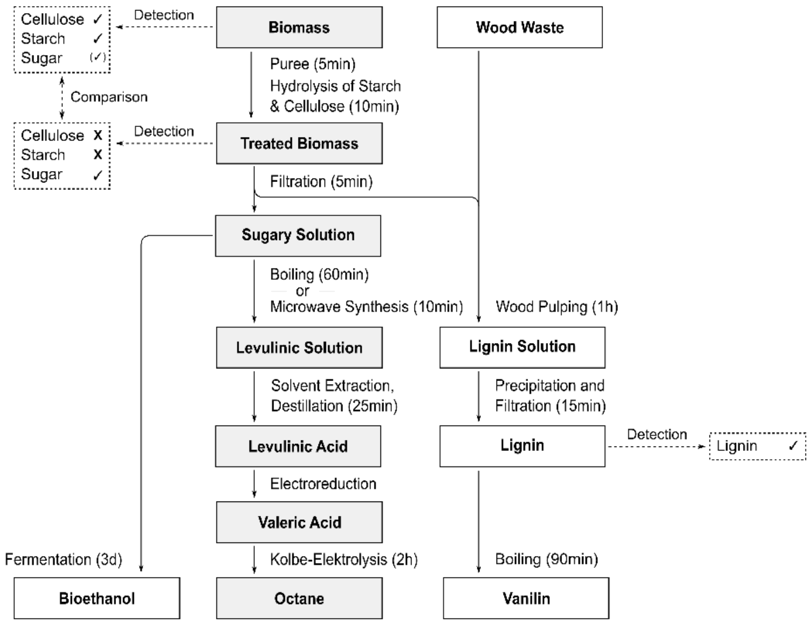

Figure 2: Possible modules of the teaching unit.

Following, selected contents will be presented, embedded into an exemplary course concept (marked grey in Fig. 2) for the production of octane from biomass. Within this course, not only the development and processing of starch and cellulose from organic waste but also the subsequent synthesis of the platform chemical levulinic acid and the conventional fuel octane are being covered.

3.1 Introductory Seminar

The introductory seminar aims at establishing a theoretical basis of the essential contents as well as giving an overview of the “status quo” in the field of biomass conversion. In order to activate students’ prior knowledge, their thematic associations such as well-known concepts (*e.g.* E10), applications (biodiesel, fertilizer) and processes (fermentation of biomass) are collected, structured in a mind map and explained if necessary. Based on the inquiry results (see above), first generation biofuels are most likely to be mentioned by the majority of students. These statements can thus serve as a starting point for the (ethical) discussion of the use of cultivable land for fuel production, which may be initiated by the teacher based on newspaper or internet articles. During the debate, the question of how this problem can be solved is likely to arise. In this case, attention can be drawn to leftover biomass, which is usually considered as waste material. Consequently, the follow-up question arises, which possible uses other remaining waste biomass with energetic constituents (cellulose, starch) possesses. This question is then to be examined in the laboratory course.

3.2 Laboratory Course

During the laboratory part, the conversion of biomass to octane is focused. Depending on the teachers’ needs and time available, the experimental procedures for the extraction of starch and cellulose as well as the subsequent hydrolysis into sugar can either be provided to the students or looked up in an internet research. However, within the first experiment, cellulosic bio-waste (here: corn residue) is pureed in order to increase the surface area. The pulp often contains both cellulose and starch; by boiling the mass for ten minutes with diluted hydrochloric acid, the glycosidic bonds are being broken and monosaccharides are being obtained. The completion of the reaction can be verified by means of detection reactions for cellulose (iodine-zinc chloride), starch (iodine-potassium iodide) (see Fig. 4 a) and sugar (FEHLING’S reagent). Since plants also contain small amounts of glucose, the Fehling test is positive both before and after hydrolysis.
For the production of octane, the sugary solution is converted into a yellowish-brown solution containing levulinic acid (see Fig. 4 b) in a simple experiment. By refluxing with a diluted mineral acid, glucose is being dehydrated, forming 5-hydroxymethylfurfural (5-HMF) in an intermediate step and then hydrolyzed to formic acid and levulinic acid (see Fig. 3) [9].

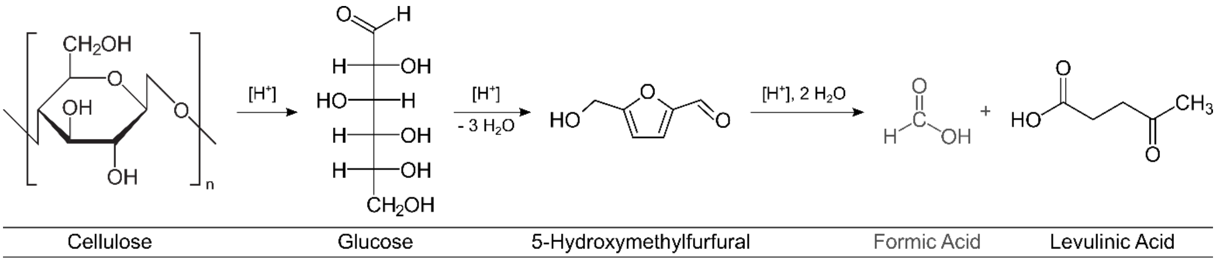

Figure 3: Reaction path from cellulose to levulinic acid.

The resulting brown humic substances are filtered off. Subsequently, the synthesized levulinic acid can be extracted from the aqueous phase with diethyl ether (see Fig. 4 c). Afterwards, the solvent is distilled off, leaving levulinic acid (90 % purity) as a yellowish, viscous liquid in the flask. The detection is carried out in chemistry class by means of an iodoform test, during which yellow iodoform precipitates, if positive (see Fig. 4 d).

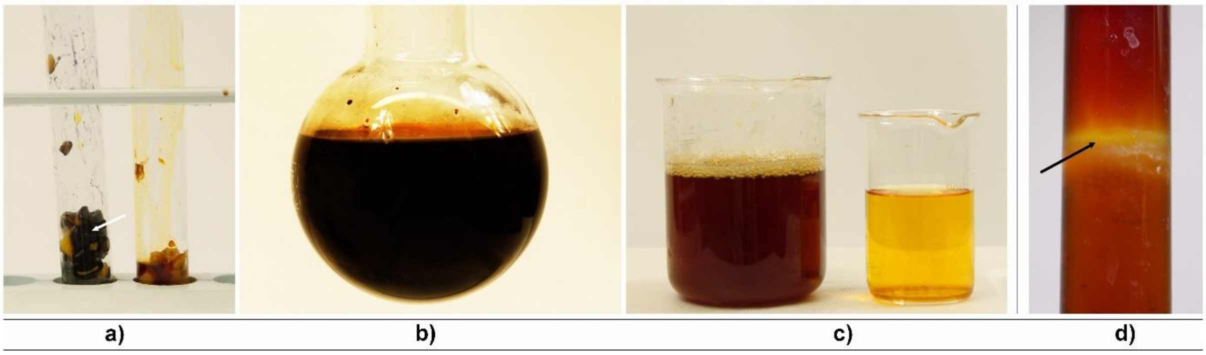

Figure 4: a) left: positive detection of starch before hydrolysis; right: negative result after hydrolysis; b) levulinic acid solution; c) aqueous phase (left) and organic phase with levulinic acid (right) after extraction; d) positive iodoform test.

The platform chemical levulinic acid, which is obtained in huge amounts as a by-product in the paper industry, can subsequently be electrochemically reduced to valeric acid [2]. The generation of valeric acid can be recognized after a few minutes by its characteristic smell. Finally, it can be converted into octane by means of a two-hour KOLBE-electrolysis, the n-octane being formed by decarboxylation and dimerization of the hydrocarbon radicals. For this experiment, either research results from SCHRÖDER [2] or a detailed description adapted for school chemistry education reported by OETKEN, QUARTHAL and FRIEDRICH [10] can be used.

3.3 Results and Discussion

The third section aims at combining both theoretical and experimental findings. Within an open discussion, students can not only debate but also reflect and assess the opportunities and risks of biomass conversion into conventional fuels from multiple perspectives (*e.g.* science, sustainability, industry, environment). Should this technology be supported in the future or are there other, probably more promising alternatives? To what extent can fuels derived from biomass satisfy the (global) fuel needs? Which arguments can persuade both industry and customers to choose sustainable biofuels over cheaper fossil fuels – especially in emerging and developing countries? Since this topic is related to some of the main challenges our society has to face in the future, many more questions are possible. During preparation, each group collects arguments and facts by means of an internet research or a WebQuest, which are subsequently combined into stance cards. These serve as a basis for the final panel discussion and can furthermore be used to sustainably secure the results.

4. Summary and Outlook

This article presents a small contribution to the didactical conceptualization of biomass conversion for school chemistry education. By means of a questionnaire, students' subject-related knowledge and perspectives in this field were identified, which subsequently served as a basis for the design of experiments and teaching materials. An exemplary course for chemistry class was presented, which illustrates the whole conversion process from biomass up to octane by the means of simple experiments that can be performed by students with common equipment and chemicals. In particular, the production of levulinic acid and its further conversion to octane offers insights into current research topics in the area of ecological and sustainable chemistry. In addition, this presented teaching unit can be extended in simple ways in terms of contents and concepts – especially the cooperation with student laboratories provides a number of possibilities to address further current topics. Overall, numerous classical contents of chemistry and biology education can be interlinked during this course within a modern, socially relevant context. Lastly, a wide range of interdisciplinary references to biology, politics and ethics are offered.

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