A Biorefinery in Rotterdam with Isobutanol as Platform?

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ENVIRONMENTALLY DESIRABLE, TECHNICALLY POSSIBLE, ECONOMICALLY NOT (YET) FEASIBLE

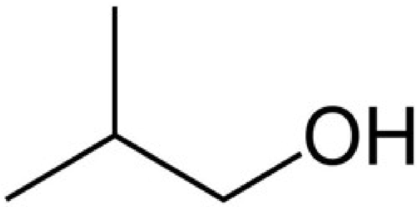

Fig 1: *Isobutanol molecule*

The port area of Rotterdam with its concentration of chemical and petrochemical industry is an important contributor to the emission of CO_2 in this country. The Rotterdam Climate Initiative (RCI) aims to reduce the CO_2 emission in 2025 by 50% compared to 1990 levels. The use of biomass as a raw material for the production of bio-based chemicals to replace fossil-based chemicals is indispensable in reaching this goal. This paper describes the assessment of the economic, technical and ecological feasibility of an isobutanol based complex in the Rotterdam harbor area.

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ISOBUTANOL

Isobutanol (**Fig 1**) is a platform molecule that can be used for a variety of chemical intermediates, such as rubbers, solvents, fuel additives, such as the diesel additive Glyceryl tert-butyl ether (GTBE), or liquid fuels such as high grade jet fuels. It is a naturally occurring product of fermentation and is found in products such as bread and Scotch whisky. But it is usually produced by the carbonylation of propylene, followed by hydrogenation. Recently a modified yeast has been developed, which ferments carbohydrates almost exclusively to isobutanol instead of ethanol. Dehydration to 2-methylpropene (isobutylene or isobutene) makes isobutanol into a versatile platform molecule. Isobutanol can be further processed into other high-value hydrocarbon products using (modified) conventional petrochemical catalytic processes. Commercial use is currently limited but it has begun to attract considerable interest as a potential additive in gasoline. It has a number of advantages over other common alcohols used for improving octane rating such as poor miscibility with water and a low freezing point. Isobutanol is widely regarded as feedstock for the production of C_4 olefins via established dehydration chemistry.

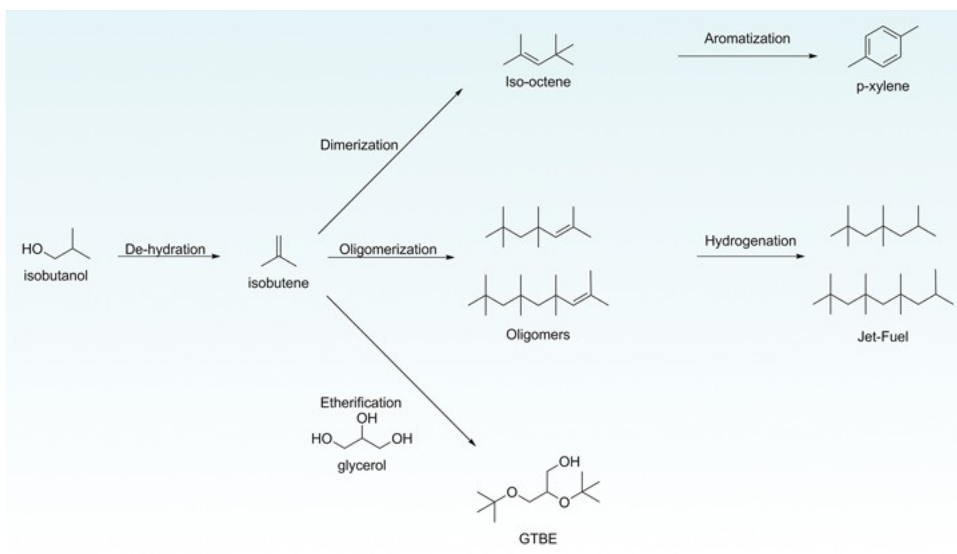

Fig 2: *Basic chemicals obtained via isobutanol dehydration. Isobutylene market: rubbers and p-Xylene market (e.g. PET)*

THE ISOBUTANOL VALUE CHAIN.

Our target molecule can be produced from different raw materials that contain polysaccharides, which can be fermented into isobutanol. Collaboration between agro, chemical and energy companies is a key to the establishment of new value chains for the bio-based economy. A new biorefinery concept has to be designed, involving novel conversion and separation technologies, along with new side streams of marketable

**The Consortium,
Iso Butanol Platform Rotterdam (IBPR)**

The IBPR consortium has been established to develop a value chain around isobutanol in the Rotterdam area. It consists of Suiker Unie as a biomass supplier, SkyNRG as a client for bio jet fuels, Indorama as a client for p-xylene, GTBE Company as a client for isobutanol itself, and AVR as a client for the waste streams. In addition, ECN supplies the chemical conversion and petrochemical processes know-how, Wageningen UR concentrates mainly on the biochemical conversions, and the TU Delft on all of them. Economic assessments are mostly performed by the company Zirk-Tech whereas the Life Cycle Assessments are performed by Utrecht University. The IBPR is led by Deltalinqs, which is supported by the Port of Rotterdam. The consortium has recently joined the umbrella of the BE-Basic consortium. Financial support was obtained from AgentschapNL, Rotterdam Climate Initiative and the Province of Zuid-Holland.

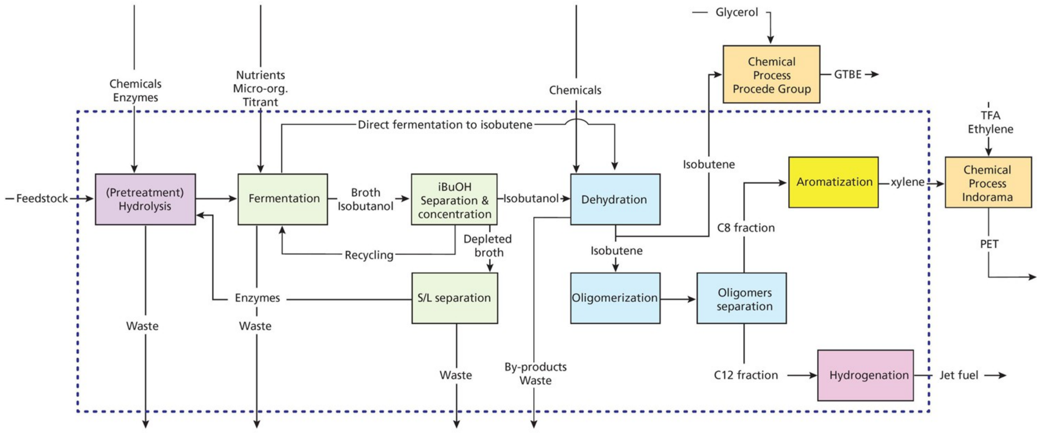

Fig 3: *Block diagram of the process developed, including an alternative option with direct fermentation of isobutylene*

products. For each part of the value chain, interested companies have to be found that can adopt it, can invest in it, and can generate sufficient value from it. Universities and knowledge institutes supply the missing know-how and insights.

SUGAR BEETS AS RAW MATERIAL

Abolishment of the EU sugar quota in 2017 will enable Suiker Unie to increase its beet processing capacity in The Netherlands. Dutch sugar beet is a sustainable feedstock due to its high sugar yield per hectare. Both crystalline beet sugar and 'thick juice' (sugar syrup) are potential fermentation feedstock for isobutanol production, just like they are already in the production of bio-ethanol. The value chain of sugar production from sugar beet in The Netherlands has existed for more than a century, and therefore beet sugar has been the first feedstock choice within the IBPR consortium. Other, potentially cheaper, non-food biomass resources are also being investigated.

Beet-sugar factories produce beet pulp as a by-product in quantities similar to the produced sugar. This pulp contains proteins, and is therefore useful as cattle feed. Most of the dry matter in the pulp, however, consists of cellulose, hemicellulose, and pectin. These must be pretreated before they can be fermented by yeast. Conventional methods to convert straw and woody biomass into fermentable sugars cannot be used for beet pulp, since these raw materials contain lignin but no pectin. Pectin hydrolyzing enzymes have not yet been developed at a price and activity level of cellulose or hemicellulose-hydrolyzing enzymes. An efficient beet pulp treatment process should also include steps to recover the proteins which could then be sold as feed components.

FERMENTATION

We envision that the isobutanol platform molecule is produced from biomass by fermentation. Taking glucose ($C_6H_{12}O_6$) as model carbohydrate, the maximum stoichiometric yield to isobutanol ($C_4H_{10}O$) from the carbohydrate is 0,41 g/g:

$$C_6H_{12}O_6 \rightarrow C_4H_{10}O + 2\ CO_2 + H_2O$$

Experimentally, 0,35 g/g has been reported so far, with the losses being primarily microbial growth and by-products. Based on the reported yields of ethanol that are close to the stoichiometric maximum for ethanol of 0,51 g/g, we believe that about 0,40 g/g should be achievable for isobutanol. Yeasts will tolerate ethanol up to levels exceeding 100 g/L. Isobutanol is however more toxic to the cells, and achieved levels are only about 22 g/L. In-situ product removal and recovery has been developed to increase the total concentrations and to continue the fermentation. Additional genetic engineering of the isobutanol producing yeast is required to use all monosaccharides (arabinose, galacturonic acid, xylose etc.) obtained from beet pulp hydrolysis and not just glucose. To date, this has not yet been demonstrated at any significant scale.

DOWNSTREAM CHEMISTRY

Several catalytic steps are required to produce the desired products (**Fig 2**). Catalytic dehydration of isobutanol to isobutylene can be done analogous to existing commercial dehydration processes for tertbutanol and ethanol. Subsequent oligomerization and aromatization steps have been described, but require further development to become commercially feasible. The oligomerization of isobutene to the C_{12} and C_{16} molecules used to be the undesired reaction in the production of iso-octene from isobutene. The reaction can be tuned to yield this fraction, but this is not practiced commercially at large scale and thus needs to be demonstrated. The hydrogenation of the C_{12}/C_{16} fraction is not expected to be a major hurdle, as polishing hydrogenation is practiced widely in the fuel industry. p-Xylene from either isobutene or a C_8 olefin has also been described, but yields are around 30 % and the exact reaction sequence is subject to debate. There are no bottlenecks in the production of Glyceryl tertbutyl ether from isobutene, as this is the preferred and envisioned route to GTBE.

LOGISTICS

Several logistic scenarios are possible. Sugar thick juice or sugar beet pulp might be shipped to Rotterdam for processing, or beet pulp processing and fermentation might be done near the sugar factory, resulting in a much smaller volume of isobutanol to be transported to Rotterdam. The latter case would have the disadvantage of large isobutanol distillation towers and associated safety management outside petrochemical complexes. The destination of residue streams from beet pulp processing and fermentation and the potential of heat integration are other factors to be taken into account in choosing the best logistics.

PROCESS ASSESSMENT

In the base case process, the cash flow is negative for thick juice as well as for beet pulp when producing a mix of p-xylene, jet fuel and GTBE. The use of thick juice for isobutanol production is currently not economically feasible, considering the achievable yield of isobutanol as well as the raw material cost. In the case of beet pulp, the negative cash flow is mainly caused by the high cost of enzymes for hydrolysis. Producing only GTBE on the other hand has much better economics. The economic picture can be further improved by choosing products with a higher value than fuels and bulk chemicals. However, according to Life Cycle Assessment estimations, the non-renewable energy use (NREU) can be reduced by approximately 40% and 60% (compared with a fossil-based equivalent that produces the same products), when using thick juice and beet pulp, respectively. Greenhouse gas emission reductions would be 65% and 70%.

OUTLOOK

The suggested process (**Fig 3**) has no insurmountable technical hurdles, but most steps still require testing. Several steps require significant improvements, primarily the production of jet fuels and p-xylene. The production of glyceryl tertbutyl ether, however, becomes attractive when using sugar beet pulp. Enzyme costs should be reduced, which may be achieved by lower intrinsic enzyme costs, enzyme recycle scenarios, or using crude, unpurified enzyme streams, as has been suggested for cellulosic ethanol. Switching to a lignocellulosic feedstock, when efficient sugar liberation is available, could be an economically viable and sustainable alternative. A major improvement would be achieved if micro-organisms were able to convert fermentable sugars directly into isobutene. This would eliminate the complex isobutanol purification. Currently, there are companies developing such micro-organisms. **Fig 3** includes also this option. ❑

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