A Pathway towards Carbon Neutral Fuels: Synthesis of Iso-butanol with Renewable Methanol

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In Germany, the mobility sector contributes about 16% of total CO_2 emissions [1]. In order to reach German climate goals, these emissions have to be reduced by 80-95% from their 1990 levels by the year 2050 [2]. Yet in 2008, worldwide transportation gave rise to 25% of global energy related CO_2 emissions [3]. Therefore, transitioning towards carbon neutral fuels has a high potential in decreasing global CO_2 emissions, which explains the great interest in using bio feedstock for the synthesis of alternative fuels in recent decades. Usually, the approach was to use abundant carbon sources such as cellulose, starch, and lignine and to transfer them by catalytic or biological processes into useful products [4]. Unfortunately, biomass based resources come with a number of issues. The main issue is its vast area needs leading to the "*Tank vs.Teller*" discussion [5,6]. In order to overcome the rivalry for land use of fuels and food, second and third generation fuels have been developed, which are not competing with the food production on the same land area [7]. For decades, bioethanol has been presented as a substitute or additive for fossil fuels in internal combustion cars. However, depending on the production, more energy is needed than will be provided from the synthesized bioethanol [8,9]. In higher concentrations (>15%) as additive, the fuel mixture requires physical changes to the consumer's car. This would lower the consumer acceptability and the speed at which this new fuel could replace fossil fuels. It is, therefore, necessary to produce a fuel that – in order to be carbon neutral - is based on CO_2 and produced with regenerative energy. In short, this concept is called Power to Fuel (PtF). Here, methanol is synthesized from hydrogen originated from water electrolysis and CO_2 [10]. Because methanol as such in general cannot be used in the existing car fleet as fuel, it has to be upgraded into higher alcohols that can be used as a substitute for gasoline. A first starting point for converting methanol into higher alcohols is the homologisation to ethanol and further upgrading into 1-butanol, which also tackles the disadvantage of a lower caloric heating value of ethanol and its high hydrophilicity, as well as the corrosive properties [11]. A useful reaction sequence is the Guerbet-reaction. It was developed by Marcel Guerbet in 1899 [12]. In this reaction, alcohols are dehydrogenated on a heterogeneous catalyst and converted via cross- and homo aldol condensations into the corresponding coupling products. It is believed that these products are then re-hydrogenated at the same catalyst and thus it is described as a hydrogen borrowing mechanism. The main product of this reaction sequence is 1-butanol and a lower amount of higher, mostly branched Guerbet-alcohols, that arise from subsequent condensation reactions [13]. Today costs of ethanol based 1-butanol (~1,60$/kg) as fuel are too high because of the low selectivity towards 1-butanol [14]. With regard to selectivity and educt composition, it seems reasonable to use the very similar C-methylation protocol of Siddiki et al. to methylate ethanol with methanol to iso-butanol [15]. It promises a high iso-butanol selectivity due to the hindrance towards subsequent reactions [16,17]. In addition, iso-butanol exhibits up to 60% lower maximum soot volume production in non-premixed counter flow flames than 1-butanol [18]. Due to the intensive ongoing research in the past decade on the Guerbet-reaction [17], knowledge about the catalyst systems shall be transferred to the methylation of ethanol, in order to lay the foundations for an economically viable process for carbon neutral fuel production.

In an autoclave under autogenous pressure, ethanol reacts with methanol. Carbon and alumina supported transition metal catalysts will be used to aid the base catalyzed methylation of ethanol to iso-butanol. Variation of the transition metal will be correlated to the d-band center of these metals in order to compare the results to the findings of Riittonen and colleagues, who found a dependence of hydrogen-metal interaction on conversion [19], and was correlated by Wu et al with the downshift of the d-band center [13]. Using carbon supported catalysts allows for a more direct comparison because of the far weaker metal support interaction compared to alumina based catalysts. The information will be used to formulate multi-metallic catalysts. Triflates (Triflouromethansulfonates) of several rare earth and transition metals are used as water-stable Lewis acids for activation of the carbonyl group, in order to reveal the influence of Lewis acidic functionalities of supports in the catalyst. Through variation of reaction conditions, like base concentration, educt composition and temperature, insight into process dependencies will be gathered.

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