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PRODUCTION OF JET AND DIESEL FUELS FROM SYNGAS

Final Report for CRADA No. PNNL/312 with LanzaTech, Inc.

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Executive Summary

This project was a collaboration between PNNL and LanzaTech, Inc. to leverage expertise in China in the production of advanced biofuels. LanzaTech has recently developed a novel path involving CO fermentation that converts CO gas, with or without H_2, to 2,3-butanediol (BDO). The objective of the project was to develop thermochemical processes to convert the BDO to jet and diesel fuels so that an integrated process to convert syngas to infrastructure compatible transportation fuels could be designed. The primary focus was on the production of isoparaffins (similar to synthetic paraffinic kerosene), but routes to aromatic fuels were also evaluated.

There are several different direct and indirect pathways to fuels from the BDO feedstock. Indirect routes could involve initial dehydration to either methyl ethyl ketone (MEK) or methyl vinyl carbinol (MVC, or 1-butene-3-ol) intermediates. MEK can be converted to 2-butanol, which can in turn be converted to butenes or fuels. MVC is an intermediate to butadiene, which could be oligomerized to hydrocarbon fuel precursors.

In studies conducted by PNNL, direct conversion of BDO over zeolitic solid acid catalysts produced aromatics, but catalyst lifetimes were too short to be industrially practical. MEK as a feed gave the same results as BDO, likely a result of MEK being an intermediate in BDO conversion.

Much better results were obtained by the indirect conversion to fuels through 2-butanol as an intermediate. In this process, BDO is initially dehydrated to MEK, which is then hydrogenated to 2-butanol. These two processes were successfully integrated into a single unit operation allowing 90% aqueous BDO (from BDO produced by LanzaTech) to be converted to 2-butanol in high yield. 2-Butanol was separately converted over H-ZSM-5 to either aromatics or to linear and branched olefins depending on processing temperature. At 400 °C, aromatics were produced without loss of catalyst activity for over 5 days. C5 to >C12 olefins were produced at 250 °C and a mixture of aromatics and olefins were produced at 300 °C. Hydrotreating the olefin products produced at 250 °C would provide a jet-range blendstock of linear and isoparaffins. The demonstrated BDO to 2-butanol process could easily be further integrated with either a fuel-forming step to make jet blendstock or with a dehydration step to produce butenes as chemical products.

Preliminary testing identified several potentially viable catalysts for the conversion of BDO to 1,3-butadiene. The best catalysts were analogs of thoria, the only previously known catalyst for this transformation, and comprised early transition metal or lanthanide oxides. All of the rare-earth oxides (with the exception of promethium, which is a radioactive element) and other oxide and mixed oxide materials were synthesized or obtained as commercial products. One catalyst material tested maintained activity and selectivity over 7 reruns in the pyroprobe apparatus used for micro-scale catalyst testing. BDO conversions over the series of runs ranged from 94% down to 49.1% with 1,3-butadiene selectivity as high as 65.7% and as low as 33.3%. Limited flow reactor testing verified activity for butadiene formation, but further testing is needed to attain conversions and selectivities observed in small scale catalyst screening.

Techno-economic analyses indicated that cost-competitive biorenewable hydrocarbon fuels from biomass are within reach given the various assumptions made. Given these assumptions, it appears that the estimated production costs are between \$3 and \$4/gallon of jet blendstock. These costs are preliminary, they have not been optimized for full integration across the entire process, and assumptions have not been validated experimentally.

The life cycle GHG emissions for bio-based jet fuel and petroleum-based jet fuel, along with the relative contribution of each stage were determined. Bio-based jet fuel emissions are 1.6 g CO_2-e/MJ fuel, a reduction of 98% from petroleum-based jet fuel at 88.1 g CO_2-e/MJ. The primary reason for this large reduction in emissions is that the conversion process produces power, which is assumed to be exported to the grid, effectively counting as an emissions credit (negative carbon emissions) due to the displacement of fossil power production (assumed average U.S. grid mix). Because biomass is considered a carbon-neutral feedstock, the amount of carbon that is emitted during fuel combustion is essentially the same as that taken up from the atmosphere during plant growth, and therefore, only fossil carbon is accounted for in the analysis.

The results of the TEA analysis are significant because the overall process of gasification of biomass, fermentive conversion of syngas to products, and conversion of those products to hydrocarbon fuels produces a fuel within a reasonable estimated cost range. All of the carbon in the biomass is used, including the lignin, which contributes to the favorable cost estimates. Further cost savings might be realized as further process improvement, integration, and optimization occur.

Further work is needed to advance the technologies demonstrated in this project. Conversion of BDO to 2-butanol has been demonstrated, but optimization of the processing conditions and water content of the feed is needed. Catalyst lifetime with aqueous feeds needs to be determined. Optimal catalyst activation methods are required to maximize intermediate and product yields. Integration of the 2-butanol forming process with the fuel forming step or the dehydration step to butenes would provide routes from BDO to a range of fuels and chemical products. Further testing and development of catalysts for conversion of BDO to 1,3-butadiene are needed. Some of this work could be conducted on a 30 cc (of catalyst) scale. Mass and carbon balances would be better defined and sufficient quantities of fuels and products could be produced for property testing.

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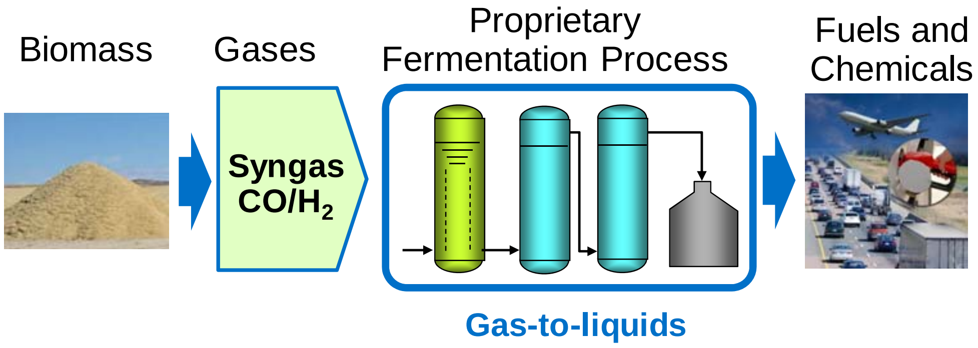
1 Introduction

This project was a collaboration between PNNL and LanzaTech, Inc. to leverage expertise in China in the production of advanced biofuels. LanzaTech, incorporated in the US, has subsidiaries and facilities in China and is focused on making biofuels and chemicals from syngas (Figure 1). LanzaTech is partnering with Chinese entities to build two demonstration facilities for ethanol by fermentation. LanzaTech has recently developed a novel path involving CO fermentation that converts CO gas, with or without H_2, to 2,3-butanediol (BDO), in contrast to previous studies in which BDO was prepared by fermentation of hexoses and pentoses (Long 1963; Voloch 1986).

Figure 1. LanzaTech biomass to fuels and chemicals process.



The objective of the project was to develop thermochemical processes to convert the BDO to jet and diesel fuels so that an integrated process to convert syngas to infrastructure compatible transportation fuels could be designed. The primary focus was on the production of isoparaffins (similar to synthetic paraffinic kerosene), but routes to aromatic fuels were also evaluated.

There are several different direct and indirect pathways to fuels from the BDO feedstock (Figure 2). Indirect routes could involve initial dehydration to either methyl ethyl ketone (MEK) or methyl vinyl carbinol (MVC, or 1-butene-3-ol) intermediates. MEK can be converted to 2-butanol, which can in turn be converted to butenes or fuels. MVC is an intermediate to 1,3-butadiene (1,3-BD), which could be oligomerized to hydrocarbon fuel precursors.

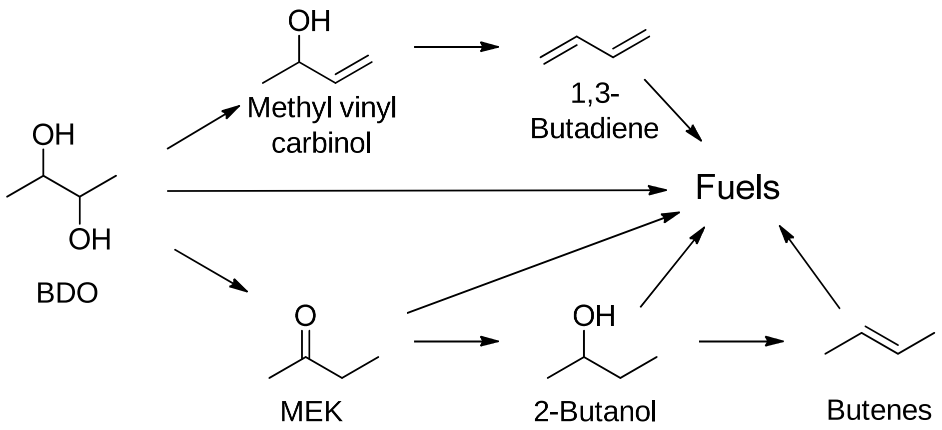


Figure 2. Direct and indirect pathways to fuels from BDO.

Catalyst testing and process development involved initial screening in batch and flow systems. Down-selected catalysts or processing conditions from the screening were further tested in packed-bed continuous flow reactors. Techno-economic evaluations were conducted to guide development efforts and to assist with down selection of process options.

Work was conducted in two stages. In the first stage, preliminary techno-economic analysis (TEA) based on literature processes was conducted (Task 1a). In addition, screening of catalysts for the various pathways for conversion of BDO to fuels occurred (Task 2). A decision was made on May 4, 2011 based on the results of Tasks 1 and 2 as to which pathway(s) to fuels held the most promise. Task 3 occurred in the second stage, in which down-selected pathways and catalysts were studied in a lab-scale flow reactor (1-5 cc) to define conversions, yields, catalyst lifetime, and fuel quality. Life cycle analysis (LCA) was conducted with experimental data in Task 1b.

2 Experimental

2.1 Materials

Methyl ethyl ketone (99+ %) and 2,3-butanediol were obtained from Aldrich Chemical Co. The Aldrich BDO (98%) was a mixture of meso- (~76%) and racemic d/l isomers (~24%). BDO obtained from LanzaTech was a d/l mixture (~95%) and contained very little meso isomer (~3%).

2.2 Pyroprobe GC/MS Apparatus

A pyroprobe unit was used in this work for micro-scale (1-5 mg) catalyst testing. The unit used was a CDS Analytical, Inc. Series 5000 pyroprobe (model 5200). The pyroprobe was equipped with a downstream heated catalyst bed (not always used in these experiments), and a heated Carbopack adsorbent bed located between the catalyst bed and the gas chromatograph (GC) inlet, used to temporarily sorb products prior to analysis. The GC used was an Agilent Technologies 7890A GC system, equipped with an Agilent Technologies 5975C inert XL mass spectroscopic (MS) detector with Triple-Axis Detector. The GC column used for product separation was a J &W DB-5MS, 30 m x 0.25 mm column.

2.3 Catalyst Screening Procedure Using the Pyroprobe GC/MS Apparatus

The feedstock used for this screening campaign was 10 wt% BDO (Aldrich) in deionized (DI) water. The catalyst (~2mg of powder) was loaded into a quartz tube (25 mm long x 1.9 mm I.D.; open at both ends), and held in position using a quartz wool plug on both ends of the powder layer. Approximately 1 µL of feed solution was subsequently dispensed onto the back quartz wool plug then loaded into the pyroprobe wand with the liquid-containing end down, so that upon heating the liquid feed vapors would be carried through the catalyst bed. After the tube was loaded into the pyroprobe wand, the end of the wand was inserted into the pyroprobe unit and sealed. Helium carrier gas flowed through the probe wand and over the quartz wool plugs and catalyst. Upon initiation of the unit, a heating coil encircling the quartz tube, rapidly heated the tube and its contents to the test temperature and maintained it at that temperature for usually 15 seconds. Carrier gas flows were typically 20 ccm of He through the pyroprobe. Reactant and product vapors were rapidly carried out of the quartz tube and adsorbed onto a Carbopack bed at 40 °C, then later desorbed from the adsorbent bed at 300 °C. The desorbed products were carried into the GC/MS unit for separation and analysis. Area % reports were generated for % conversion of BDO and product selectivity to 1,3 butadiene, methyl vinyl carbinol, MEK, and isobutyraldehyde (IBA). Aldrich BDO was a mixture of d/l and meso isomers. Early analyses integrated over both isomers (reported as BDO) until method improvements allowed separate quantification.

2.4 Continuous Flow Reactor

A laboratory-scale (1-5 cc), continuous fixed bed flow reactor was constructed to investigate chemical conversions on a scale larger than the pyroprobe with control of feed rates, temperatures, and pressures. An isocratic HPLC pump was used to introduce liquid feeds, including BDO, MEK, and 2-butanol. The reactor was made of stainless steel tubing with ¼" outer diameter and 8" length. The catalyst bed was positioned approximately in the middle of the tube, held in place by quartz wool plugs and 80-100 mesh Pyrex glass beads, both above and below the catalyst bed. The packed reactor tube was placed approximately in the middle of an electrically heated furnace. The furnace control thermocouple was located on the outside skin of the reactor tube, adjacent to the catalyst bed. A mass flow controller was used to control nitrogen, air, or H_2 carrier gases at flow rates up to 1000 sccm. The system also included two chilled receiver vessels for collecting liquid product samples alternately without disturbing the experiment. The reactor pressure was maintained with use of a back pressure regulator. Effluent gas rates were measured with a soap bubble flow meter and stopwatch and gas samples obtained using a gas-tight syringe. Gas samples were analyzed on a Carle Series 400 AGC using the # 160-Sp application (refinery gas analysis). Liquid samples were analyzed on an Agilent 6890 GC with an FID detector or on the Agilent GC/MS described above. The process flow diagram is shown in Figure 3.

2.5 Rare-Earth Oxide Catalyst Preparations

The rare-earth oxide catalysts with the exception of Promethium and Cerium were prepared by the thermal decomposition of their hydrated nitrate salts. Decomposition temperatures varied from 450 ^{o}C to 850 ^{o}C. The respective metal nitrate decomposition temperatures (Table 1) were found in the literature (Wendlandt, 1956; Wendlandt, 1960; Haire). The nitrates were generally calcined for 2 hours at the listed decomposition temperatures to form the listed oxides (Table 1). Commercial Ce oxide powders were obtained from sources within PNNL.

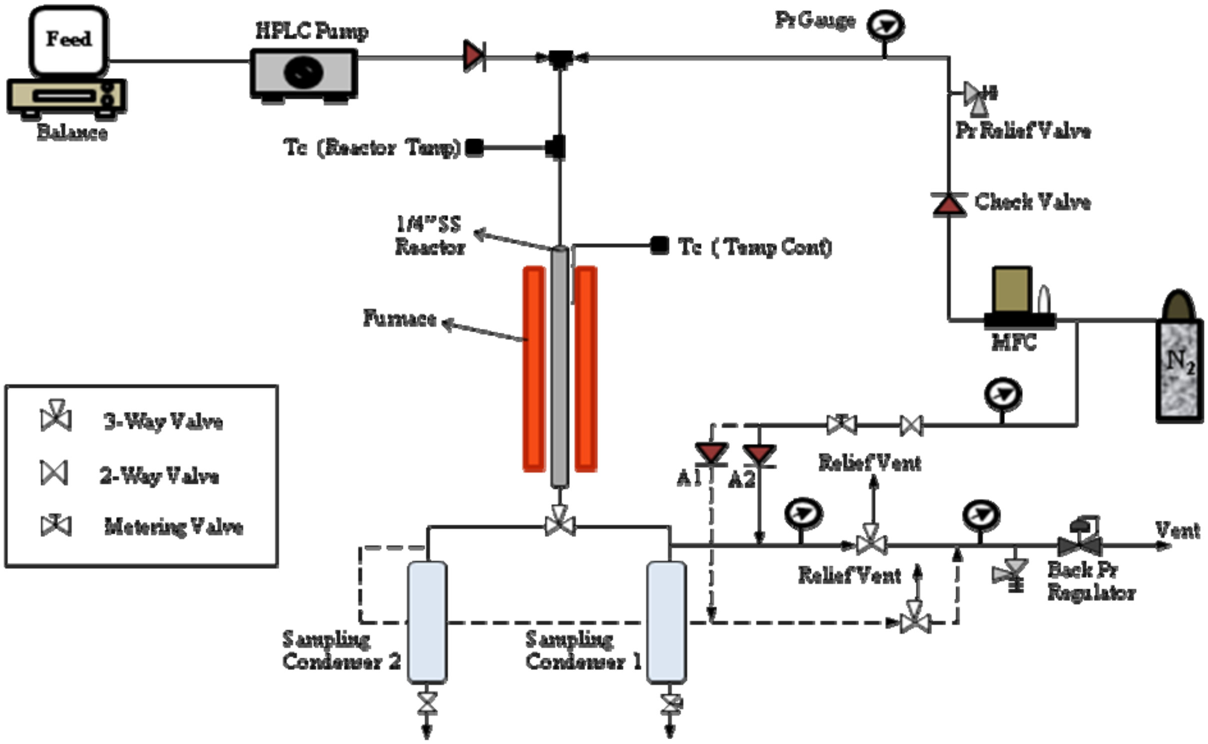


Figure 3. Process flow diagram to study the conversion of BDO and MEK to higher hydrocarbons

Table 1. Nitrate decomposition temperatures in rare-earth oxide syntheses

Rare-earth Oxide	Nitrate Decomposition Temperature (°C)
La_2O_3	850^{o}C
Pr_6O_{11}	550^{o}C
Nd_2O_3	850^{o}C
Sm_2O_3	750^{o}C
Eu_2O_3	800^{o}C
Gd_2O_3	800^{o}C
Tb_4O_7	450^{o}C
Dy_2O_3	800^{o}C
Ho_2O_3	650^{o}C
Er_2O_3	650^{o}C
Tm_2O_3	650^{o}C
Yb_2O_3	750^{o}C
Lu_2O_3	600^{o}C

2.6 Rare-Earth-Like Oxides and Other Oxide Preparations

Several rare-earth-like oxides, such as yttrium oxide, scandium oxide, and zirconium oxide were also synthesized by thermal decomposition of the hydrated nitrate salts. The oxide phases that were prepared and the corresponding nitrate decomposition temperatures are listed below (Table 2).

Table 2. Nitrate decomposition temperatures in rare-earth-like oxide syntheses

Rare-earth-like Oxide	Nitrate Decomposition Temperature (°C)
Y_2O_3	500^oC
Sc_2O_3	550^oC
ZrO_2	600^oC

Hafnium oxide, HfO_2, was prepared by precipitating the hydrous oxide from a solution of hafnium chloride using an aqueous ammonia solution. The precipitate was washed, dried, and calcined at 600 ^oC prior to use.

A 50% ZnO/50% SiO_2 catalyst was prepared by mixing a zinc nitrate solution with a silica sol, drying the mixture, and calcining the resulting solids at 600 ^oC for 2 hours.

An $Al_{0.75}Zn_{0.25}O_x$ catalyst composition was prepared that had previously been reported (Bhattacharyya, 1963). The method used to prepare the catalyst was a co-precipitation procedure that was devised in-house. A first solution containing dissolved ammonium carbonate was added to a second solution containing dissolved aluminum nitrate and zinc nitrate. The resulting precipitate was DI water washed, then dried and calcined at 600 ^oC for 2 hours.

3 Results and Discussion

Preliminary technical and techno-economic analysis results are summarized and recommendations are given in Section 3.1. Sections 3.2 through 3.5 present a more detailed discussion of technical and TEA/LCA results from this project.

3.1 Decision Point Process and Outcome

The project was structured with a “go”/”no go” decision half way through the project, at which point the technical and economic feasibility would be judged and a path forward decided. This section discusses the process that was used to decide whether the preliminary results warranted further research and, if so, to define the direction of the research in the second half of the project. The result of the decision point was “go”.

3.1.1 The Decision Process

Technical and TEA evaluations were conducted in parallel and were carried out at a high level. Technical studies were conducted to demonstrate feasibility. Most data were collected at very small scale with the objective of demonstrating whether catalysts could carry out the desired conversions. Limited experiments were conducted at the laboratory scale, but conditions were not optimized in any way. Technical success was indicated if yields to desired products were about 50% or greater, supported by a judgment that the studied catalyst could be operated successfully in a larger flow reactor. TEA studies integrated thermochemical biomass conversion to syngas, biochemical fermentation of syngas to BDO, and conversion of BDO to fuels and certain intermediate products. Detailed inputs to the model generally were not yet available so assumptions were made and sensitivity analyses conducted. TEA success was decided if conditions were found that indicated reasonable production costs could be attained. The recommendations that follow from these evaluations were based on processes that held both economic and technical promise. The various assumptions that were made helped to identify where more information or additional improvements were needed. Thus, the evaluations were used to guide the research that was conducted in Stage 2.

3.1.2 Preliminary Technical and Techno-Economic Analysis Results

Catalyst screening was conducted on a micro scale with use of a pyroprobe apparatus interfaced with a GC/MS. This apparatus allowed rapid screening of catalysts in which a feed could be passed over the catalyst at temperature and the products directly analyzed. Promising catalysts were placed in a continuous fixed-bed flow reactor or a batch reactor for screening on a larger scale. These methods allowed several pathways from BDO to fuels to be evaluated (Figure 2). A brief summary of the findings is presented. More details are found in the following sections.

Both the direct conversion of BDO to fuels and the indirect route through methyl ethyl ketone (MEK) gave similar results over zeolite catalysts, probably because MEK is a likely intermediate in BDO conversion. Both could be converted to aromatic hydrocarbon fuels with good initial activity, but for only up to about 15 h in flow reactor tests. At longer times, BDO converted to MEK, but no further. Therefore, neat feeds of these reagents are considered unlikely to be economically converted at an industrial scale over these types of catalysts and were not considered further.

Oligomerization of MEK over a basic catalyst in a batch reactor gave good conversion to dimer and trimer compounds. While not extensively studied, oligomerization of MEK is considered to be a viable pathway to fuel-range hydrocarbons.

The best conversions to fuels were obtained when 2-butanol was dehydrated and condensed over zeolite catalysts. In a flow reactor, 2-butanol can be converted to liquid isoparaffinic hydrocarbons with yields of about 90% or, at higher temperatures, to liquid aromatic hydrocarbons with yields of up to 80% without loss of activity for over one week. Presumably, this conversion takes place via the intermediacy of butenes. 2-Butanol should be readily available from BDO by the reportedly facile dehydration to MEK followed by what is expected to be an easy hydrogenation to 2-butanol under mild conditions using known technology. A single-step process for dehydration and hydrogenation would have favorable economic benefits and is considered technically feasible.

Conversion of BDO to butadiene has been determined to be feasible in screening experiments. One catalyst material tested maintained activity and selectivity over 7 reruns in the pyroprobe apparatus. BDO conversions over the series of runs ranged from 94% down to 50% with 1,3-butadiene selectivity as high as 65.7% and as low as 33.3%. Variability was not systematic and presumably represented experimental variation. Testing in a flow reactor confirmed the production of butadiene, but work is needed to attain the conversion and selectivity results of the pyroprobe apparatus. The oligomerization of butadiene to fuel-range hydrocarbons has been reported in the literature but not confirmed in this project.

The techno-economic analysis considered a process consisting of four main processing areas: gasification and syngas conditioning, fermentation, oxygenate conversion to fuels and/or products, and steam generation. For this analysis, separate conversion of ethanol and BDO were assumed, followed by combination to the final blendstock. Modeling and economic assumptions used were similar to those used in the OBP design cases (Dutta, 2011): 2000 mtpd wood, an indirectly heated gasifier, and waste heat usage for electricity generation. The economic assumptions are nth plant, 2007 USD, 10% IRR, 96% stream factor and MACRS depreciation. Given these assumptions, the estimated preliminary production costs were between \$3 and \$4/gallon of jet blendstock. However, costs were not optimized for full integration across the entire process and the assumptions have not been validated experimentally. Nevertheless, the preliminary cost estimates suggested that economically viable jet fuel blendstock production was possible.

3.1.3 Decision Point Conclusions and Recommendations

The conclusion of this analysis was that the “go”/”no go” decision should be “go”. Preliminary technical studies demonstrated the feasibility of converting BDO to fuels via an indirect route through an intermediate. The TEA analysis indicated that cost-competitive biorenewable hydrocarbon fuels from biomass were within reach given the assumptions made.

The suggested direction for Stage 2 work was to continue to examine processes for conversion of BDO to intermediates, then on to hydrocarbon fuels. The conversion of ethanol to hydrocarbon fuels is being conducted elsewhere by LanzaTech. The results of both efforts eventually will contribute to an integrated biorefinery process that maximizes biogenic carbon use.

The preliminary technical results suggested that viable intermediates to fuels include 2-butanol, butadiene, and MEK oligomers. It was recommended that Stage 2 work focus primarily on conversion of BDO to 2-butanol and conversion of 2-butanol to fuels, since this sequence gave the best results in preliminary studies. A single process step for dehydration of BDO to MEK combined with hydrogenation of MEK to 2-butanol was desired in order to minimize unit operations and capital expenses. Further work was needed on the conversion of 2-butanol to hydrocarbon fuels to increase the molecular weight and minimize lighter fractions. A smaller effort in the conversion of BDO to butadiene was recommended to further define the capability of these routes to afford fuel precursors.

A more complete discussion of Stage 1 and Stage 2 results is presented in the following sections.

3.2 Direct Conversion of BDO to Fuels

The direct conversion of polyols to hydrocarbons with zeolite catalysts tend to form aromatics. For example, glycerol, reported by T. Hoang and R. G. Mallinson from University of Oklahoma (Hoang, et. al., 2010), tended to produce aromatics over three dimensional pore zeolites, for instance, HZSM-5, HZSM-11, and HY zeolites. In contrast, H-Mordenite did not form aromatics, but rather produced formaldehyde, acetaldehyde, and acetol.

In our work, the direct conversion of BDO to hydrocarbons was attempted over H-ZSM-5 catalyst. In practice, it was found that the product distributions for experiments using either BDO or MEK as pure feeds were nearly identical, suggesting that MEK is the likely intermediate in BDO conversion. The results of both experiments are shown in Table 3. In a typical experiment, 1.28 g of H-ZSM-5(30) (Si/Al = 30, Al_2O_3 binder) was loaded into a ¼ inch tube reactor. The feed rate was 0.05 mL/min and the reactor was heated to 400 °C. Samples were collected over a period of 75 h. As can be seen in Table 3, the catalyst was only active for about 6 h for the production of hydrocarbons. After that, the catalyst was only active for BDO dehydration to MEK. It is believed that coke formation changed the selectivity of the catalyst. While it is possible to continuously regenerate the catalyst, for example in a side stream removed from a fluidized bed reactor, this mode of operation is not optimal. This consideration in combination with the observation that this process would form aromatics, rather than the desired isoparaffins, prompted a focus for the remainder of the work on indirect methods via MEK derivatives (such as 2-butanol) or butadiene. The possibility that mixed composition BDO/EtOH feeds would show different selectivities than the pure BDO feed was not explored.

Table 3. Comparison of the product distribution using either BDO or MEK as pure feed over H-ZSM-5(30)/Al_2O_3 catalyst in the continuous reactor.

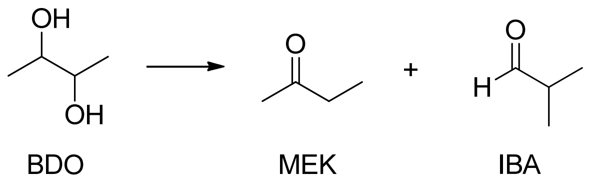
	BDO			MEK		
Products	**3.0 h**	**6.0 h**	**18 h**	**3.5 h**	**6.1 h**	**16 h**
MEK	0.0	24	49	0.0	24	57
Benzene	5.5	0.0	0.0	6.3	1.1	0.0
Toluene	15	5.5	0.0	30	7.4	0.9
Xylene	24	15	0.0	30	15	3.0
Naphthalenes	14	1.9	0.0	10	3.4	0.0

3.3 Indirect Conversion of BDO to Fuels Through MEK

This section discusses results of experiments to convert BDO to MEK, oligomerization of MEK, MEK to 2-butanol, and 2-butanol to hydrocarbons.

3.3.1 The Conversion of BDO to Methyl Ethyl Ketone (MEK)

MEK may be produced by dehydration of BDO with acidic catalysts. The reaction mechanism involves the acid catalyzed pinacol rearrangement in which initial dehydration is followed by a hydride shift. A side reaction is the shift of a methyl group instead of hydride to form isobutyraldehyde (IBA). The extent to which this side reaction occurs depends on temperature and the steric environment in the intermediate carbocation.



In the literature, homogeneous aqueous solutions containing approximately 50 g/L of BDO and 0.48-1.9 M H_2SO_4 were used at 148 and 180 °C (Emerson, 1982). Yields of MEK exceeding 90 mol % were consistently obtained. In the absence of water, it was reported by Neish et al. (1945) that strong acids catalyze the formation of the cyclic ketal. Acid catalyzed aldol condensations can also be noted in relatively dry conditions.

The pinacol rearrangement can also occur with solid acid catalysts. It was reported by Lee, et al. (2000) that a 70% BDO solution in water over H-ZSM-5 catalyst can produce a large amount of MEK at 150-200 °C, but with a poor catalyst lifetime. This was likely caused by dealumination in the aqueous solution.

A study with acidic alumina catalyst was reported by Kannan (1969). The dehydration of d/l- and meso-BDO at 235 and 400 °C yielded MEK as the major product. IBA was a less prominent product at lower temperatures, with more being observed at higher temperatures.

3.3.1.1 Catalyst Screening for Conversion of BDO to MEK in the Pyroprobe Apparatus

The pyroprobe was used to conduct small scale qualitative catalyst screening to determine feasibility and suggest the direction of research in larger scale equipment. Experiments were run in three ways: (1) with catalyst in the heated pyroprobe, (2) with an inert support in the pyroprobe and the active catalyst in a small heated post-reactor, and (3) with catalyst in both the pyroprobe and post-reactor. Each experiment discussed in this section used commercial BDO obtained from Aldrich.

In a typical experiment using catalyst in the pyroprobe, 2 mg of H-ZSM-5(30) was loaded in the pyroprobe and 1 µL of 10% BDO in water was injected onto the catalyst. The probe was heated rapidly to either 300 or 500 °C for 15 sec. Helium carrier gas (20 mL/min) was used to sweep the product onto a trap for collection (trap temperature = 40 °C). The product was desorbed (340 °C for 2 minutes) and transferred to a GC/MS injector (Agilent 7890A GC, split ratio = 100/1, initial temperature = 40 °C, hold for 5 min, final temp = 250 °C, hold for 3 min, carrier gas = 1mL/min He). The MS detector was an Agilent 5975C.

At 300 °C, the reaction achieved 97.3 % BDO conversion with 78.6% selectivity to MEK, 10.5% isobutyraldehyde, 1.1% butane, and 3.4% acetic acid. At 500 °C, the BDO conversion was close to 100% with 56% MEK and 40% aromatics. No aldol condensation products were observed. The background reaction of BDO over various supports such as SiC, silica, TiO_2 and ZrO_2 and quartz wool were qualitatively checked in the pyroprobe. For quartz wool, the BDO was 25.8% converted to a mixture of MEK (major product) and IBA. With silica gel as catalyst, 95% BDO conversion with 8% butadiene and 85% of MEK and IBA were observed. Y-zeolite, 10% Ni-ZSM-5, and 10% Fe-ZSM-5 at 500 °C did not form a significant amount of MEK. Na-ZSM-5 (with 20% ZrO_2) generated MEK, IBA, and some acetaldehyde.

In the second configuration, 25 mg H-ZSM-5(30) was loaded into the post reactor and 1 µL of 10% BDO was loaded onto quartz wool in the pyroprobe. The probe was heated to 300 °C under a flow of He (20 mL/min) and the BDO vapor was passed into the post reactor, also at 300 °C. The BDO conversion was near 100% with MEK as the major product. Other products detected by GC/MS included hydrocarbons and aromatics. The product in the gas phase included propane, butane, butenes, pentene, 1,2-dimethylpropane, MEK, and IBA.

In another experiment, 2 mg of H-ZSM-5(30) was loaded into the pyroprobe and 25 mg of the same catalyst was loaded in the post reactor. 1 µL of 10% BDO in water was injected onto the catalyst in the pyroprobe. The probe was heated to 500 °C for 15 second and the post reactor was heated to 300 °C. In this two stage catalytic reactor, BDO was 100% converted to mostly aromatics with some C3 and C4 hydrocarbon gases also formed.

The mixed oxide $PrCeO_x$ was tested in the pyroprobe with 1 µL of 10% BDO in water as feed. The probe was heated to 400 °C. The BDO conversion was about 40% with ethanol, acetaldehyde, acetic acid, acetone, epoxides, and ketals being detected as products. It appears that $PrCeO_x$ functioned primarily as an oxidation catalyst, cleaving the vicinal diol.

3.3.1.2 Convert BDO to MEK with H-ZSM-5 in a Parr reactor

2 g of H-ZSM-5(30) and 150 mL of BDO (Aldrich) were loaded into a 300 mL Parr reactor. The reactor was purged with N_2 then heated to 300 °C for 4 h, reaching a final pressure of 1750 psig. The BDO conversion was 57% and the liquid products included 15.8% MEK, many aldol condensation products, the dioxolane ketal (product of BDO and MEK condensation) (Figure 4). Many cracking products were found in the gas phase, with the gas analysis showing about 30% propane, 9% butane, 11.5% butane, 1% pentene, 3% 1,2-dimethylcyclopropane, 11% IBA and 36.5% MEK. 10 mL water were added to the products in the Parr reactor and heated to 300 °C for another hour (Figure 5). Ketals were reduced in concentration and the BDO and MEK in the solution phase increased to 61.6% and 23.8%, respectively, suggesting that the ketal was converted back to the starting material and MEK by hydrolysis.

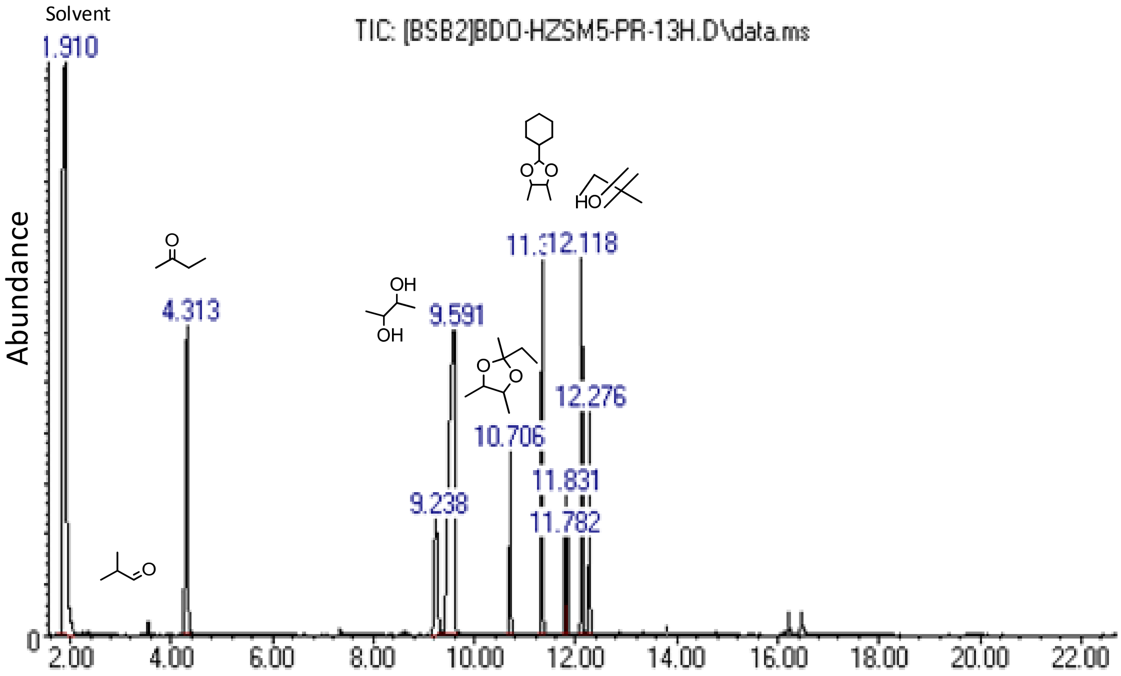


Figure 4. BDO and H-ZSM-5 heated to 300 °C for 4 h in Parr Reactor

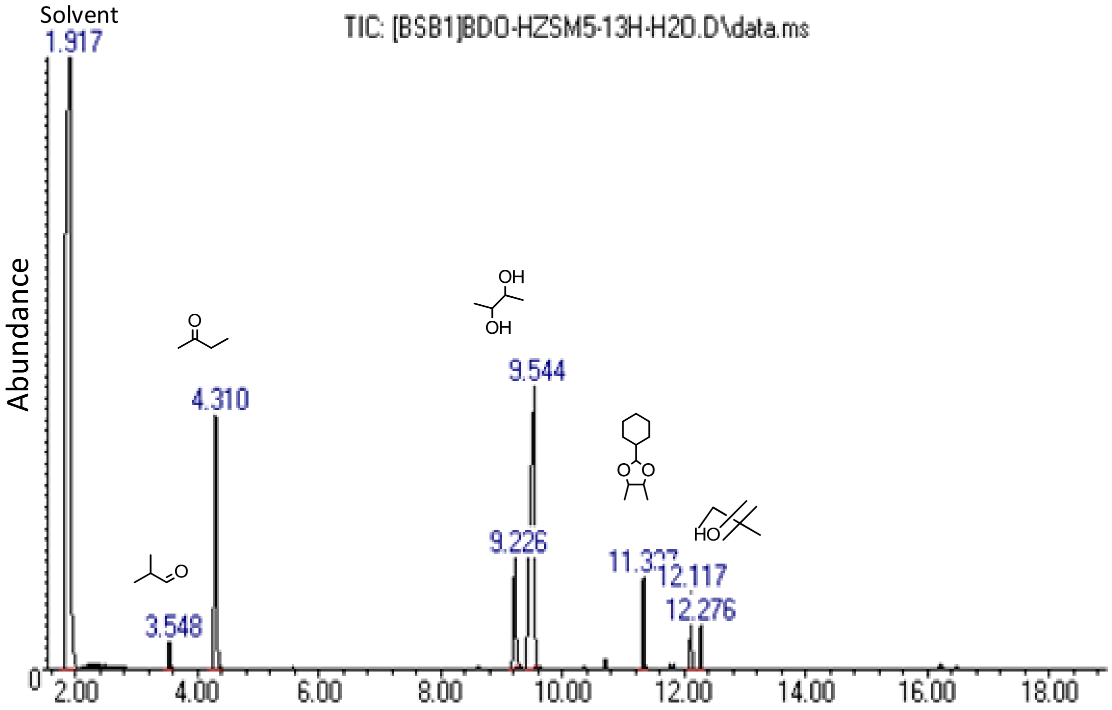


Figure 5. Water added to the product in the above figure heated for 1 h at 300 °C

3.3.1.3 Convert BDO to MEK in a Continuous Flow Reactor

Initial experiments were conducted with pure BDO rather than an aqueous BDO solution because it was felt that water would eventually deactivate the catalyst by dealumination. Selectivity to MEK in the anhydrous feed was found to be low, however, because condensation reactions were favored. Later experiments used aqueous solutions of BDO, leading to much higher selectivities to MEK and IBA. Dealumination could be minimized by use of an appropriate water concentration.

In the first exploratory experiment, 1.2 g of H-ZSM-5(30) was loaded into the flow reactor. Pure Aldrich BDO was used as feed with a feed rate of 0.05 mL/min and the reactor was heated to 300 °C. Samples were collected over the 92 h time-on-stream (TOS) experiment and results are shown in Table 4.

Table 4. Conversion of BDO to MEK over H-ZSM-5(30) catalyst in the flow reactor at 300 °C.

Sample	TOS (h)	Color	MEK	IBA	Butadiene	Products BDO	Aromatics	Naphthalene	C8
1	3	brown	0.84	0	-	-	62	14.2	1.6
2	6	brown	23.9	5.2	2.1	-	31.9	1.9	6.9
3	17.5	brown	48.9	15.4	5.4	-	-	-	13.2
4	21.75	brown	57.1	17.8	4.1	-	-	-	5.5
5	25.5	lt brown	-	-	-	-	-	-	-
6	42	yellow	72	25	-	-	-	-	-
7	50	yellow	80	15	-	-	-	-	-
8	67.8	yellow	-	-	-	-	-	-	-
9	74	yellow	52	19.1	-	3	-	-	-
10	92	lt yellow	-	-	-	-	-	-	-

At the beginning of the experiment, the H-ZSM-5(30) was very active in producing aromatics. The catalyst also produced numerous condensation products (Figure 6); C8 condensation products are shown in Table 4. However, the catalyst lost activity quickly and at 3 h TOS the formation of aromatics ceased and MEK and isobutyraldehyde (IBA) became the dominant products. Condensation products might have promoted coke formation, but this could not be confirmed in this experiment.

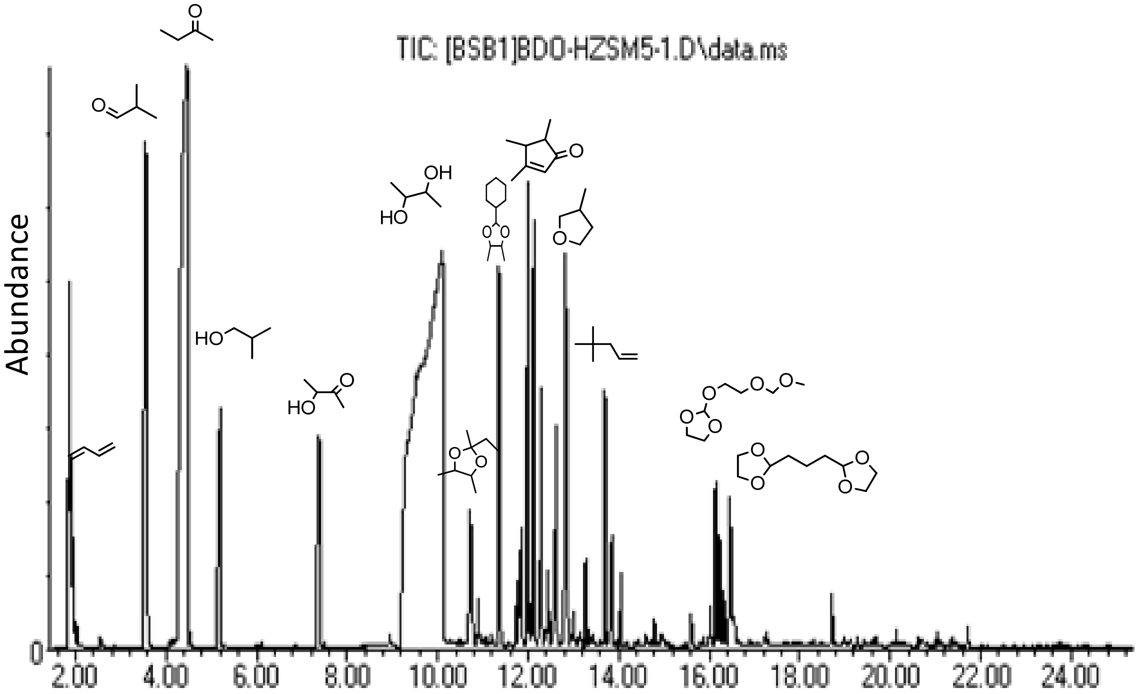


Figure 6. 100% BDO with H-ZSM-5(30) catalyst in the continuous flow reactor at 300 °C

When the pure BDO was replaced with 50% BDO in water in the continuous reactor run, the MEK/IBA yield was improved and far fewer condensation by-products were formed (Figure 7). Because of the large water concentration, however, the H-ZSM-5 catalyst deactivated over time. This deactivation was likely caused by dealumination of H-ZSM-5(30) in water. An attempt to regenerate the catalyst by combustion in air (to remove coke) formed a material that could not produce aromatics, indicating the deactivation is permanent. (The performance of ZSM-type catalysts was later improved by adjusting the water concentration as discussed below.)

A series of experiments was conducted to determine the effect of temperature on conversion and selectivity over alumina (Engelhard 4126) in the continuous flow reactor using pure (Table 5) and aqueous (Table 6) BDO from LanzaTech and Aldrich. 1.5 g of Engelhard alumina was used as catalyst in each experiment. The H_2 pressure was 200 psig and the H_2 flow rate was 400 mL/min. (H_2 was used as carrier gas in the reactor because of our desire to later couple dehydration with MEK hydrogenation.) The flow rate of pure LanzaTech or Aldrich BDO was 0.1 mL/min. When 50% BDO was used (from both LanzaTech and Aldrich), the flow rate was doubled to maintain the same space velocity of BDO in the reactor. Aqueous feeds often resulted in a 2-phase product, each phase being analyzed separately.

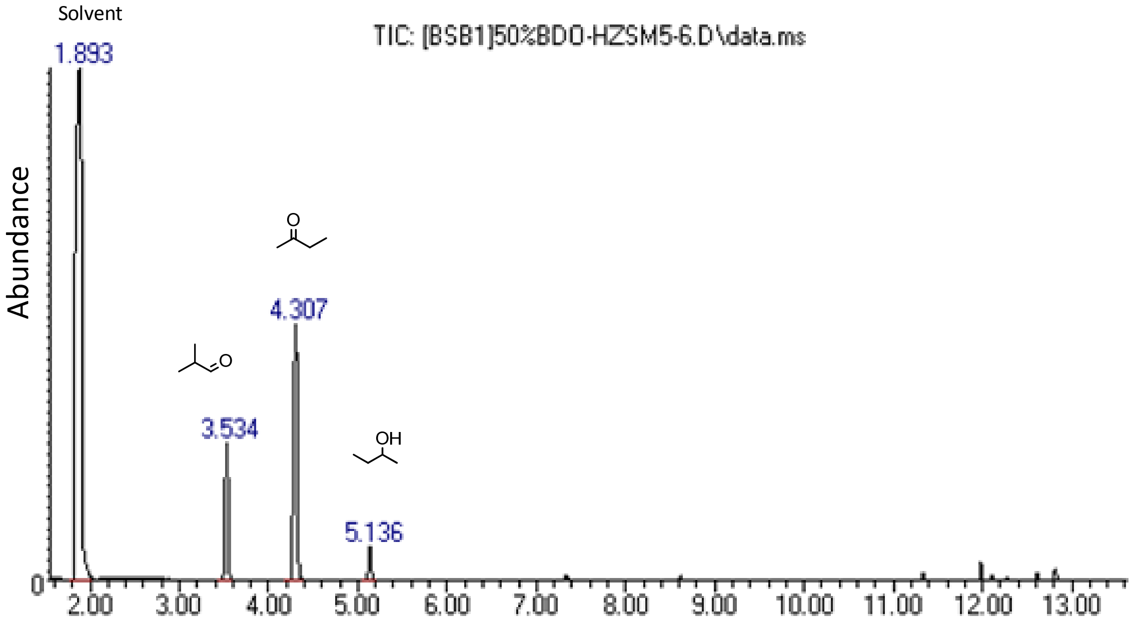


Figure 7. 50% BDO in water with H-ZSM-5(30) catalyst in the continuous flow reactor at 300 °C

Table 5. The conversion of LanzaTech and Aldrich BDO (no added water) over alumina (Engelhard 4126)

	LanzaTech BDO		Aldrich BDO	
T (°C)	MEK + IBA	BDO	MEK + IBA	BDO
300	21.8	0	20.6	0
280	25.7	0	30.8	1.3
260	14	20.8	33	1.9
240	6.3	35.4	11.3	32
220	1.9	61.4	6.1	48.2
200	1.7	65.6	3	74

Table 6. The reaction of LanzaTech and Aldrich BDO (50% in water) with alumina (Engelhard 4126). The feed rate for BDO was doubled to keep the space velocity of BDO constant.

	LanzaTech BDO			Aldrich BDO	
T (°C)	MEK + IBA	dl-BDO	meso-BDO	MEK + IBA	BDO
300 (org)	37	0	0	34.8	0
300 (aq)	36.2	21.6	1.6	56	3.8
280 (org)	38.9	7	0	36.6	0
280 (aq)	20.9	32.3	3.1	39	17.2
260 *	-	-	-	19.4	32
240 *	-	-	-	1.3	29.5
220 *	-	-	-	0	30
200 *	-	-	-	0	30
160 *	-	-	-	0	94
140 *	-	-	-	0	94

* single phase product

Over alumina, the reactivity of BDO from either LanzaTech or Aldrich was similar. The conversion of BDO to MEK occurred above about 260 °C with highest conversions above 280 °C. Like the results discussed above for H-ZSM-5(30), the selectivity to MEK was higher in the presence of 50% water.

The effect of temperature on BDO conversion for feeds containing varying water concentration over a different H-ZSM-5 catalyst than used above, H-ZSM-5(23) (Si/Al = 23, Al_2O_3 binder), was examined in the continuous flow reactor. The primary objective was to determine temperatures giving highest conversions for the various feeds. Pure Aldrich BDO, Aldrich BDO containing 50 wt% water, and LanzaTech BDO containing 10 wt% water were tested. As in the alumina experiments, the H_2 pressure was 200 psig and the H_2 flow rate was 400 mL/min. The liquid feed rate was 0.1 mL/min for both pure and 50% aqueous BDO solutions. For the 90% aqueous BDO feed solution, a feed rate of 0.06 mL/min was used.

Pure Aldrich BDO (which is mostly the meso isomer) did not begin converting until about 240 °C (Table 7). Complete conversion was not attained, even at 300 °C. For reference, H-ZSM-5(30) was found earlier to convert BDO completely at 300 °C (Table 4) indicating that the increased acidity as the Si/Al ratio decreases is important. Better conversion over H-ZSM-5(23) was observed for the 50% BDO feed (Table 8). In this case, conversion was nearly complete at 280 °C, with about 2.9% BDO remaining, and complete at 300 °C. The d/l isomer apparently converted more readily than the meso isomer as indicated by the d/l to meso ratio at each temperature. While not explicitly tested in this series of experiments, it was assumed that the catalyst deactivated with 50% water present as observed in the H-ZSM-5(30) experiments.

Table 7. The reaction of Aldrich's BDO (no added water) over H-ZSM-5(23)

T (°C)	MEK + IBA	BDO
300	26.5	21.2
280	22	42.6
260	11	56
240	4.9	78.3
220	0	90
200	0	94.5

Table 8. The reaction of Aldrich BDO (50% in water) over H-ZSM-5(23)

T (°C)	MEK + IBA	d/l-BDO	meso-BDO	(d/l) / (meso) ratio
300	88.6	0	0	_
280	59.4	0	2.9	_
260	67.2	3	14.1	0.21
240	20.6	16.6	57.3	0.29
220	2	26.3	71.7	0.37
200	0	27.5	72.5	0.38

Catalyst longevity and activity were examined in the experiment using just 10% water (90% LanzaTech BDO). Activity remained high throughout the 120.5 h (5 days) experiment (Table 9). Conversion of both d/l and meso isomers was complete at 300 °C. Dropping the temperature briefly to 280 then 260 °C resulted in decreased conversion, but raising it again to 300 °C resumed the previous activity.

Table 9. The reaction of LanzaTech BDO (90% in water) over H-ZSM-5(23); flow rate = 0.06 mL/min (table continues to the next page).

Time (hr)	T (°C)	MEK + IBA	d/l-BDO	meso-BDO
2 (org)	300	32	1.8	0
2 (aq)	300	24.3	62.9	6.5
5 (org)	300	59.9	0	0
5 (aq)	300	68.5	0	0
13 (org)	300	60.5	0	0
13 (aq)	300	74.6	2.1	0
18 (org)	300	57.7	0	0
18 (aq)	300	70.6	0	0
20 (org)	300	62.2	1.8	0
20 (aq)	300	69.5	0	0
21.5 (org)	300	60.7	0	0
21.5 (aq)	300	70	0	0
24 (org)	300	61	0	0
24 (aq)	300	69.4	0	0
27 (org)	300	63.3	0	0
27 (aq)	300	64	2.7	5.3
40 (org)	300	63.4	0	0
40 (aq)	300	66.6	0	0
43 (org)	300	62.3	0	0
43 (aq)	300	66.9	0.7	1.3
44 (org)	300	62	0	0
44 (aq)	300	67	0.1	0.1
45.5 (org)	300	63.2	0	0
45.5 (aq)	300	68	0.1	0.1
48 (org)	300	65	0	0
48 (aq)	300	60.7	2.5	0.7

Time (hr)	T (°C)	MEK + IBA	d/l-BDO	meso-BDO
49.5 (org)	300	65	0	0
49.5 (aq)	300	56.2	5.9	0.6
50.5 (org)	280	31.6	39.5	1.7
52 (org)	260	22.4	45.5	2.2
61.5 (org)	300	62.4	0	0
61.5 (aq)	300	55	17.3	1
71 (org)	300	63.7	0	0
71 (aq)	300	78.4	0.9	0
76.5 (org)	300	62	0	0
76.5 (aq)	300	66.2	0	0
86.5 (org)	300	64.9	0	0
86.5 (aq)	300	67	0	0
99.5 (org)	300	64.9	0	0
99.5 (aq)	300	63.9	0	0
112.5 (org)	300	64.5	0	0
112.4 (aq)	300	64.4	0	0
120.5 (org)	300	62.5	0	0
120.5 (aq)	300	64.5	0	0

The samples from 61.5 to 120.5 h were combined and the organic and liquid phases separated. The GC's of the aqueous and organic phases are shown in Figure 8 and Figure 9, respectively. Note that remaining BDO partitioned to the aqueous phase, ketals partitioned to the organic phase, IBA was found in both phases, and both reduced (isobutanol) and oxidized (3-hydroxy-2-butanone, and others) products were formed. An unidentified material for which no reasonable matches were obtained in the MS eluted at about 12.5 minutes. Peak identification in these and following figures was based on best matches with the MS library and was not necessarily confirmed with standards. The presence of the dimethyl ketal product requires verification, but the diluting solvent used for these samples was methanol and it may be possible this product was formed during sample preparation. The organic and aqueous phases were separately hydrogenated to 2-butanol as discussed in Section 3.3.2.2.

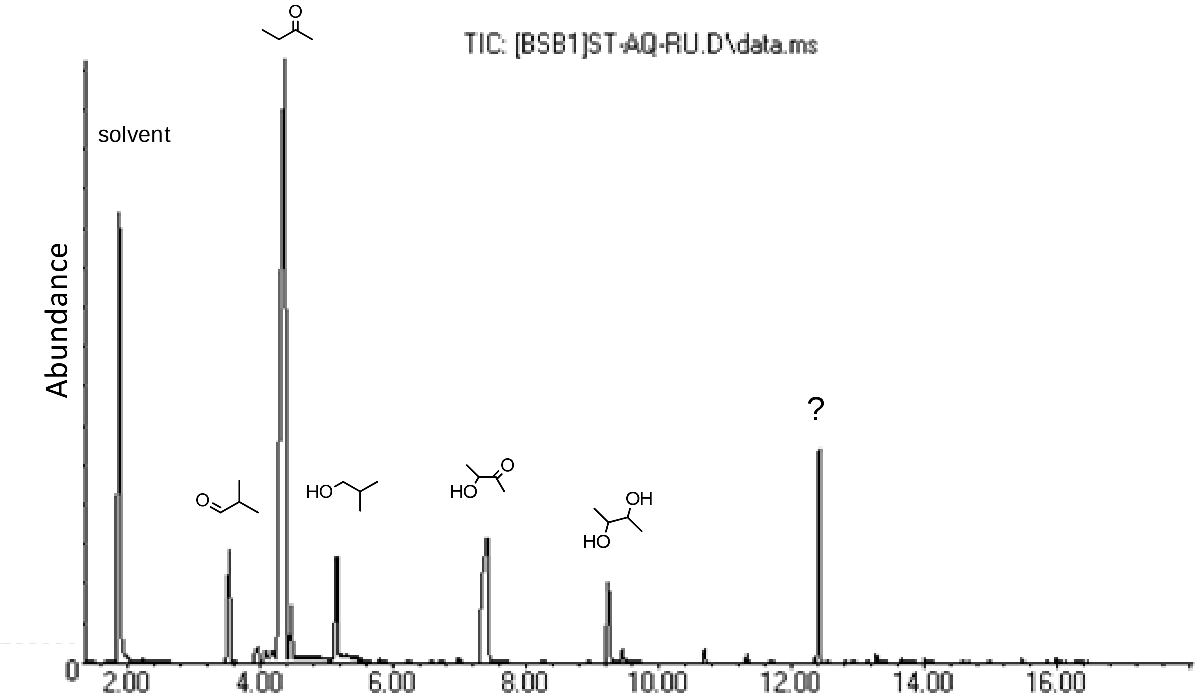


Figure 8. Combined aqueous phases of samples taken from 61.5 h to 120.5 h in the continuous conversion of LanzaTech BDO to MEK over H-ZSM-5(23) at 300 °C.

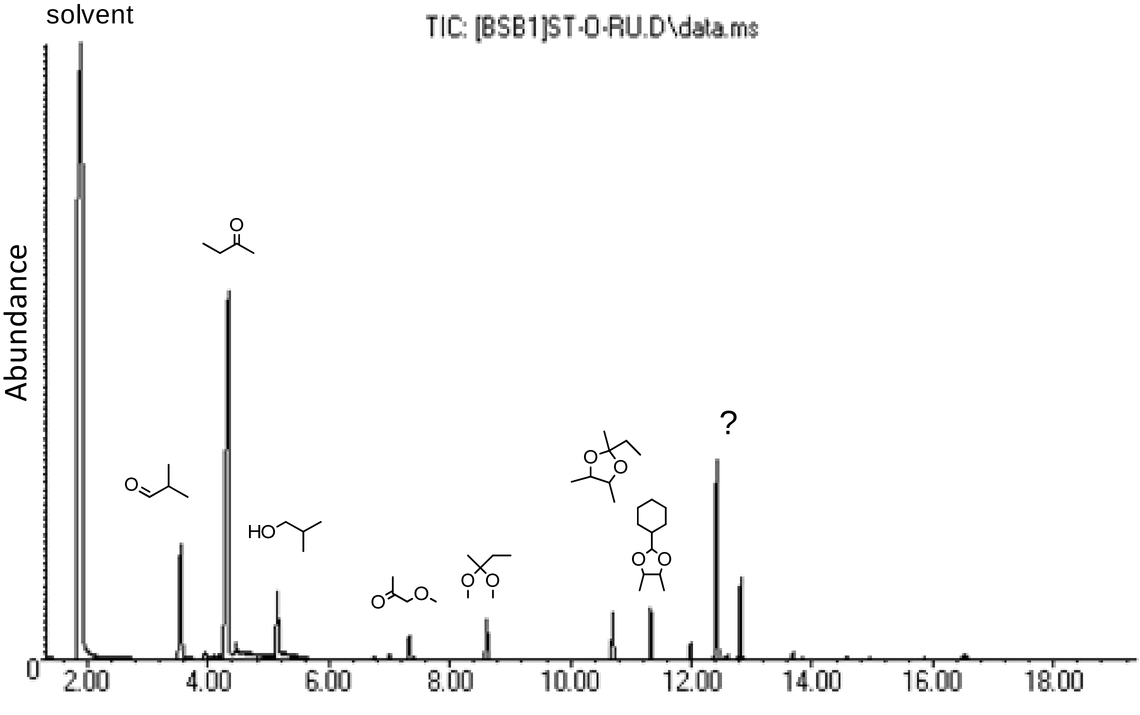


Figure 9. Combined organic phases of samples taken from 61.5 h to 120.5 h in the continuous conversion of LanzaTech BDO to MEK over H-ZSM-5(23) at 300 °C.

3.3.2 Oligomerization of MEK in the Parr Reactor

MgO/Al_2O_3 spinel (10 g) and MEK (100 g) were loaded into a 300 mL Parr reactor. The reactor was purged with N_2, heated to 300 °C, and the experiment run for 2.5 hrs. At 1 hr, the liquid had 55% MEK left and the products formed were C8 aldol condensation products of MEK as determined by GC/MS. The only compound in the gas phase was MEK. At 2.5 hrs, 43.3% MEK was left. In addition to the higher ketones formed by aldol condensation, aromatics were also detected.

3.3.3 The Conversion of MEK to 2-Butanol

The conversion of MEK to 2-butanol under mild reduction conditions has been reported (Nystrom et al., 1947). The direct conversion of BDO to 2-butanol has also been investigated (Manzer, 2010).

3.3.3.1 Hydrogenation of MEK to 2-Butanol in a Parr Reactor

The hydrogenation catalyst used for the batch reduction was 5% Ru/C (ESCAT 440, Engelhard Lot C5070 CHO1114). 5 g of Ru/C was loaded into a 300 mL Parr reactor with 100 mL MEK. The reactor was purged 3 times with H_2. It was then filled with 800 psig H_2. The reactor was heated to 100 °C and the stir rate was set to 300 rpm. The H_2 uptake happened quickly, stopping after 25 minutes. The yield of 2-butanol was over 95%

3.3.3.2 Hydrogenation of MEK to 2-Butanol in the Continuous Flow Reactor

1.5 g of 5% Ru/C (ESCAT 440, Lot C5070 CHO1114) was loaded into the flow reactor. The reactor was charged with 200 psig H_2 and a H_2 flow rate of 400 mL/min was used. A variety of temperatures between 60 and 200 °C were examined with a MEK feed rate of 0.1 mL/min. The results, shown in Table 10 and Figure 10, are consistent with the reaction being kinetically limited at 60 °C, but equilibrium limited at 200 °C. Temperatures between 120 and 160 °C gave the best yields. Pressures higher than 200 psig would tend to further increase 2-butanol formation.

1.5 g of 5% Pt/C (ESCAT238, Lot C5018 CHO1172) was loaded into the flow reactor. The reactor was pressurized to 200 psig with H_2. The H_2 flow rate during the experiment was 400 mL/min. Reaction temperatures between 40 and 280 °C were studied with a MEK feed rate of 0.1 mL/min. Samples were collected at each temperature (Table 11 and Figure 11). With 5% Pt/C, the equilibrium concentration of

Table 10. Effect of temperature on 2-butanol selectivity in MEK reduction with 5% Ru/C catalyst at 200 psig H_2

T (°C)	MEK	2-Butanol
200	25.2	62.1
180	3.9	92.9
160	1.4	97.1
140	0.87	97.3
120	0.65	97.5
100	4.8	93.7
80	7.2	92.3
60	32.2	67.3

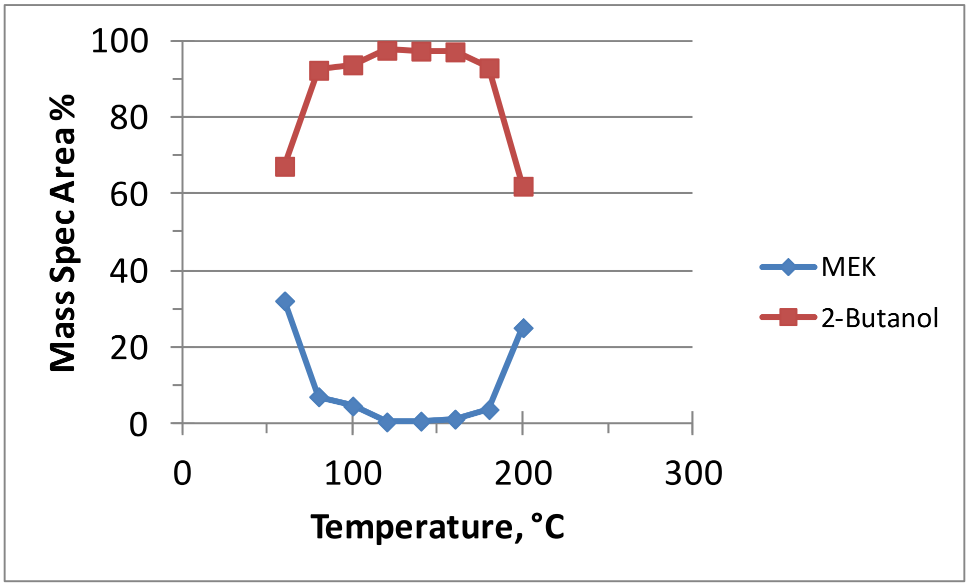


Figure 10. MEK hydrogenation to 2-butanol over 5% Ru/C at 200 psig H_2

2-butanol at 68% is lower than for 5% Ru/C. Again, higher pressures of H_2 would be required to shift the equilibrium toward the reduced product.

The experiment was repeated using 1.5 g of Raney Ni as catalyst in the continuous flow reactor. The reactor was pressurized to 200 psig with H_2 and same flow rate of 400 mL/min was used. Temperatures

Table 11. Effect of temperature on alcohol selectivity in MEK reduction with 5% Pt/C catalyst at 200 psig H_2

T (°C)	MEK	2-butanol
280	38.4	46.5
260	28.8	67.7
240	30.8	54.4
220	27.6	66
200	25.9	68.1
180	25.8	68.5
160	41.4	53.9
140	67.1	30.4
120	79.3	18.9
100	87.1	12.6
80	88.4	11.4
60	91.8	7.8
40	89	10.8

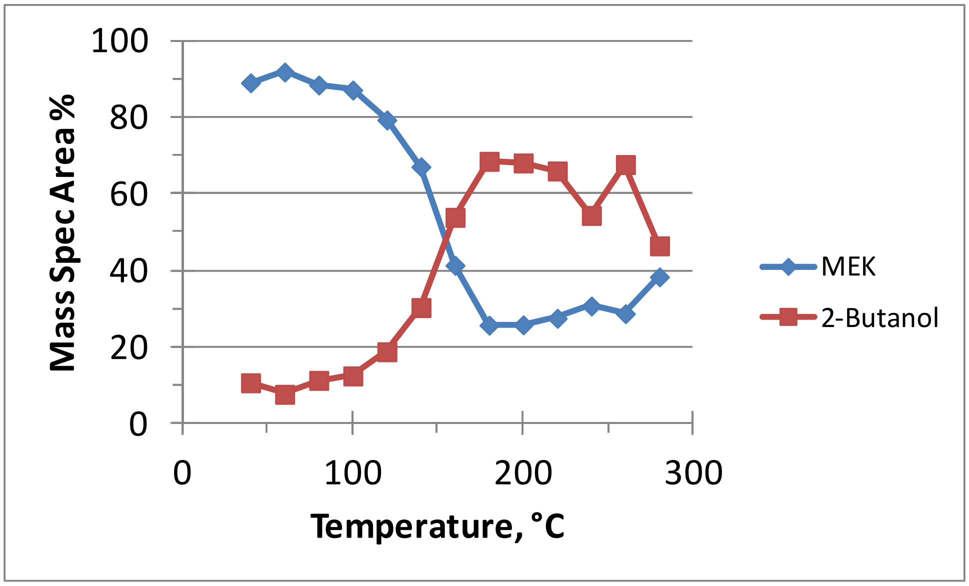


Figure 11. MEK hydrogenation to 2-butanol over 5% Pt/C at 200 psig H_2

between 40 and 220 °C were studied. The MEK feed rate was 0.1 mL/min. Solution compositions at each temperature are shown in Table 12 and Figure 12. The best results were obtained at 80 to 100 °C.

The hydrogenation of MEK to 2-butanol with Re/Ni/C catalyst (Engelhard 6818-18-1, 2.5% Re and 2.5% Ni, activated at 280 °C overnight) was also conducted in the continuous flow reactor. 1.5 g of Re/Ni/C was loaded into the flow reactor. The reactor was fed with 200 psig of H_2 at a flow rate of 400 mL/min. The experiment was conducted between 160 and 280 °C. The MEK feed rate was 0.05 mL/min, or half the rate as in the previously discussed cases. Results are shown in Table 13, Figure 13, and Figure 14. Hydrogenation is more favorable at lower temperature (Figure 13) and higher hydrogen pressure (Figure 14).

1.5% Pd/C catalyst (Engelhard) was examined for hydrogenation of MEK to 2-butanol in the continuous flow reactor. 1.5 g of Pd/C was loaded into the flow reactor. The reactor was run at 200 psig with a H_2 flow rate of 400 mL/min at temperatures between 200 and 450 °C. The MEK feed rate was 0.1 mL/min. Results are shown in Table 14 and Figure 15. The optimal temperature at 200 psig is about 260 °C, but the equilibrium concentration is only about 35%.

Table 12. Effect of temperature on alcohol selectivity in MEK reduction with Raney Ni catalyst at 200 psig H_2

T (°C)	MEK	2-Butanol
220	13.5	62
200	11.8	73.4
180	10.6	78.5
160	8.7	83.9
140	6.4	88.5
120	4.4	90.6
100	3	94
80	1.6	97.2
60	63.7	32.2
40	75.7	19.3

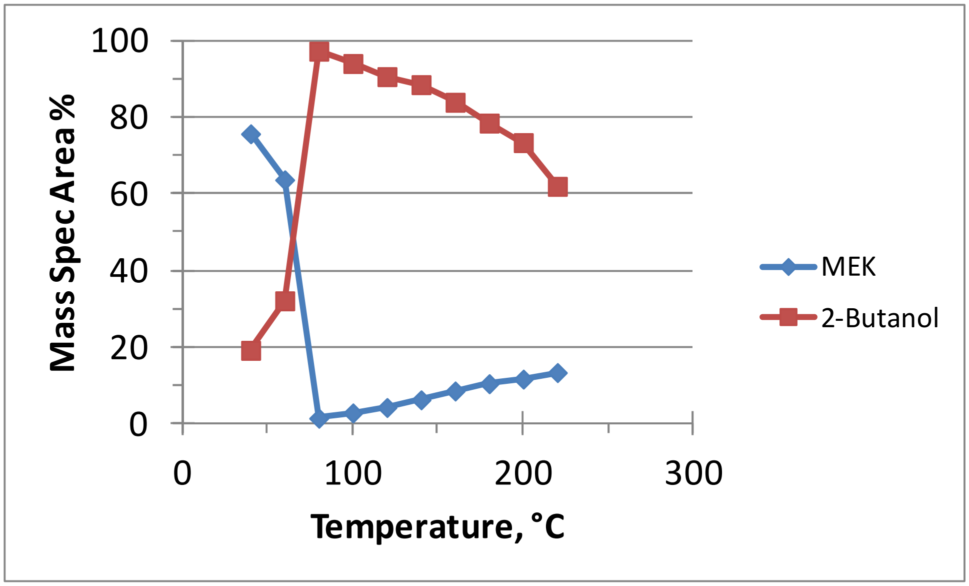


Figure 12. MEK hydrogenation to 2-butanol over Raney Ni at 200 psig H_2

Table 13. Effect of temperature on alcohol selectivity in MEK reduction with Re/Ni/C catalyst at various H_2 pressures

T (°C)	Pressure	MEK	2-butanol
280	200-180	35	52.6
240	200-180	27.3	69.2
200	200-180	18	77.8
180	200-180	14	77.6
160	200-180	11.8	81.7
220	390-360	13.9	80.5
220	200-180	18.8	76.3
220	120-100	23.8	73
220	60-50	29.4	67.6

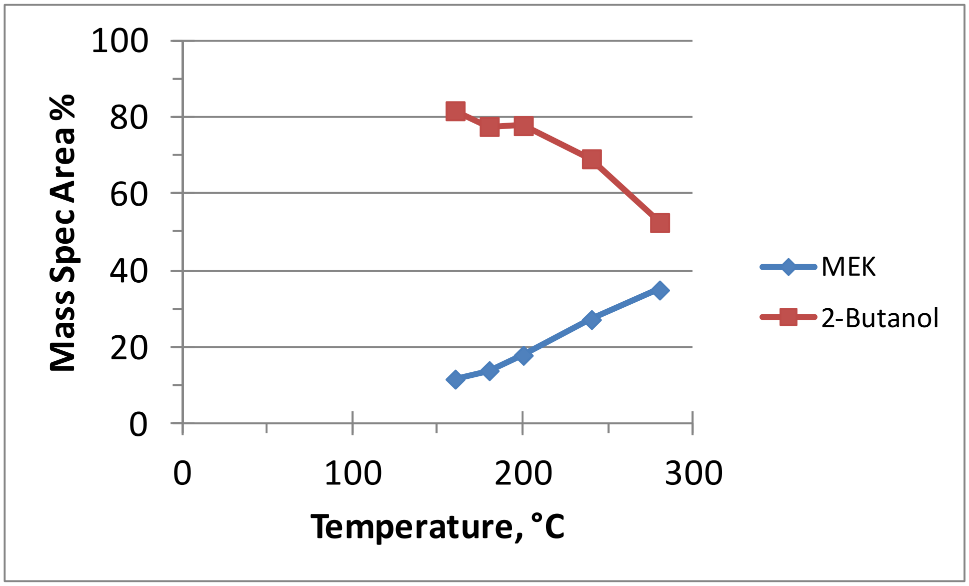


Figure 13. MEK hydrogenation to 2-butanol over Re/Ni/C at 180-200 psig

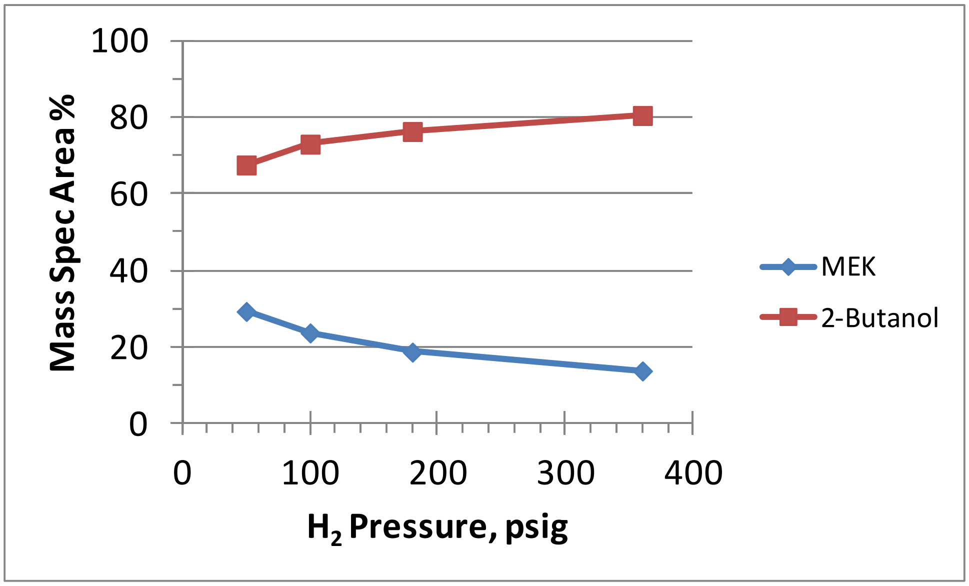


Figure 14. MEK hydrogenation to 2-butanol over Re/Ni/C at 220 °C

Table 14. Effect of temperature on alcohol selectivity in MEK reduction with 1.5% Pd/C catalyst

T (°C)	MEK	2-Butanol
450	+90	<5
400	85.4	6.8
350	73.5	14.8
300	57.7	27.3
280	54.8	30
260	49.6	34.8
240	48.3	29.4
220	50	28.7
200	45.2	10.9

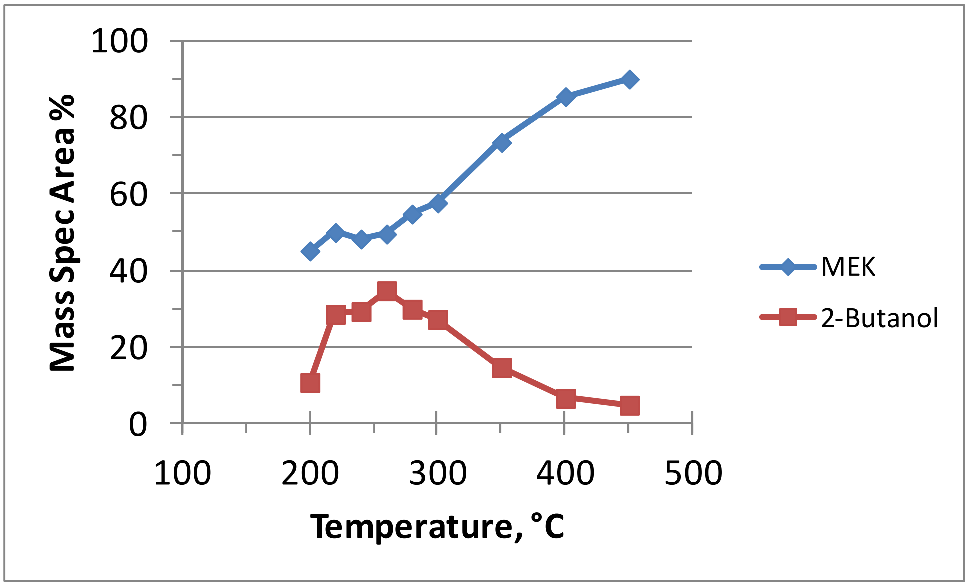


Figure 15. MEK hydrogenation to 2-butanol over 1.5% Pd/C

The samples collected from 61.5 to 120.5 h in the reaction of LanzaTech BDO (90% in water) over H-ZSM-5(23) (Table 9) were combined and the organic and liquid phases separated. These phases were separately hydrogenated to 2-butanol. The 5% Ru/C (Engelhard) catalyst (1.5 g) was tested for MEK reduction (MEK feed rate = 0.05 mL/min, H_2 feed rate = 400 mL/min, 200 psig and 160 °C) in the continuous flow reactor. The results for hydrogenation of the aqueous phase are shown in Table 15 and

Figure 16, while those for the organic phase are shown in Table 16 and Figure 17. In both cases, the combined 2-butanol + isobutanol yield was over 95%. In addition, hydrogenation of aqueous MEK samples collected in the BDO to MEK reactor between 2 and 45.5 h (Table 9) showed similar results with over 98% combined yield of these alcohols being obtained. Ketals were apparently split to BDO and MEK with the MEK being hydrogenated to 2-butanol. The unknown eluting at 12.5 min was unaffected by hydrogenation.

Table 15. Hydrogenation of the combined aqueous phases from the 61.5 – 120.5 h samples from the BDO to MEK run in Table 9 with 5% Ru/C catalyst in the flow reactor at 160 °C

TOS (h)	MEK	IBA	2-Butanol	Isobutanol	d/l-BDO	meso-BDO	% Reduction
0 (feed)	56.7	6.4	1.9	4.9	14.1	4.9	9.7
1	7.9		52.9	8.3		18.7	88.6
3	2.6		54.5	7.9		26.4	96.0

% Reduction = 100 x (2-Butanol + Isobutanol)/(MEK + IBA + 2-Butanol + Isobutanol)

Table 16. Hydrogenation of the organic phase with 5% Ru/C catalyst in the flow reactor at 160 °C

TOS (h)	MEK	IBA	2-Butanol	Isobutanol	% Reduction
0 (feed)	47.7	11.4	1	5.3	0
1	14.6	0	44.7	14.8	80.3
5.5	5.8	0	49	13.7	91.5
12.5	1.7	0	55	14.9	97.6
15.5	2.7	0	52	14.6	96.1

% Reduction = 100 x (2-Butanol + Isobutanol)/(MEK + IBA + 2-Butanol + Isobutanol)

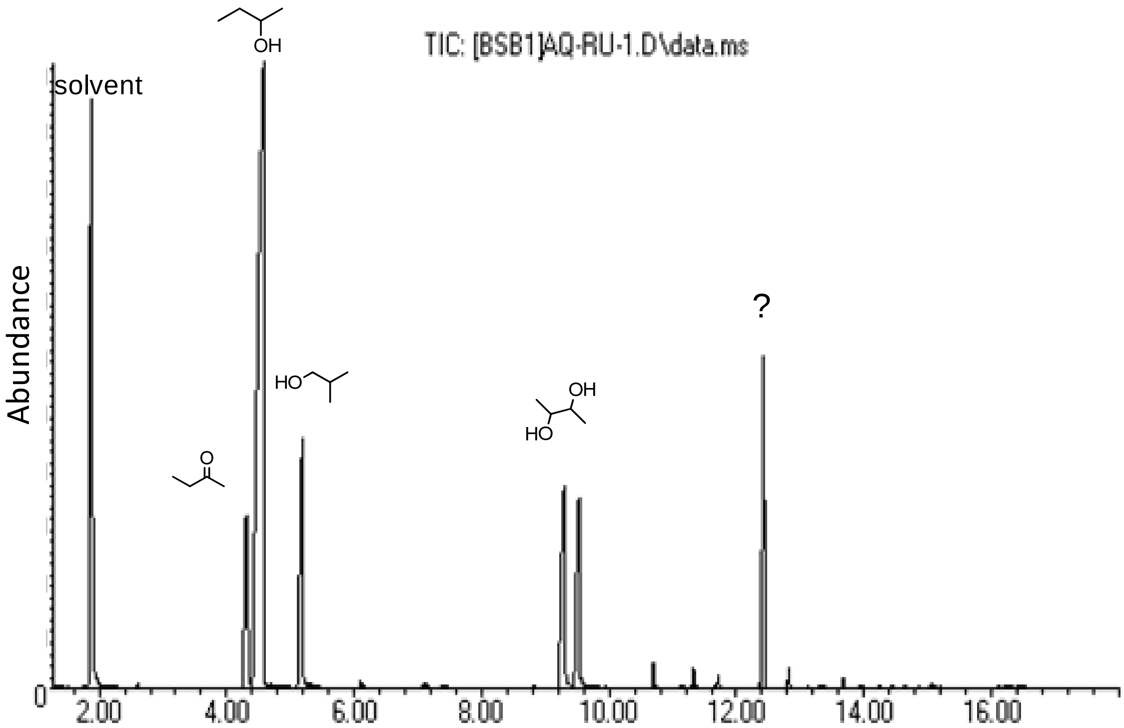


Figure 16. Reduction products using as feed the combined aqueous samples collected between 61.5 to 120.5 h in the conversion of LanzaTech BDO to MEK over H-ZSM-5(23).

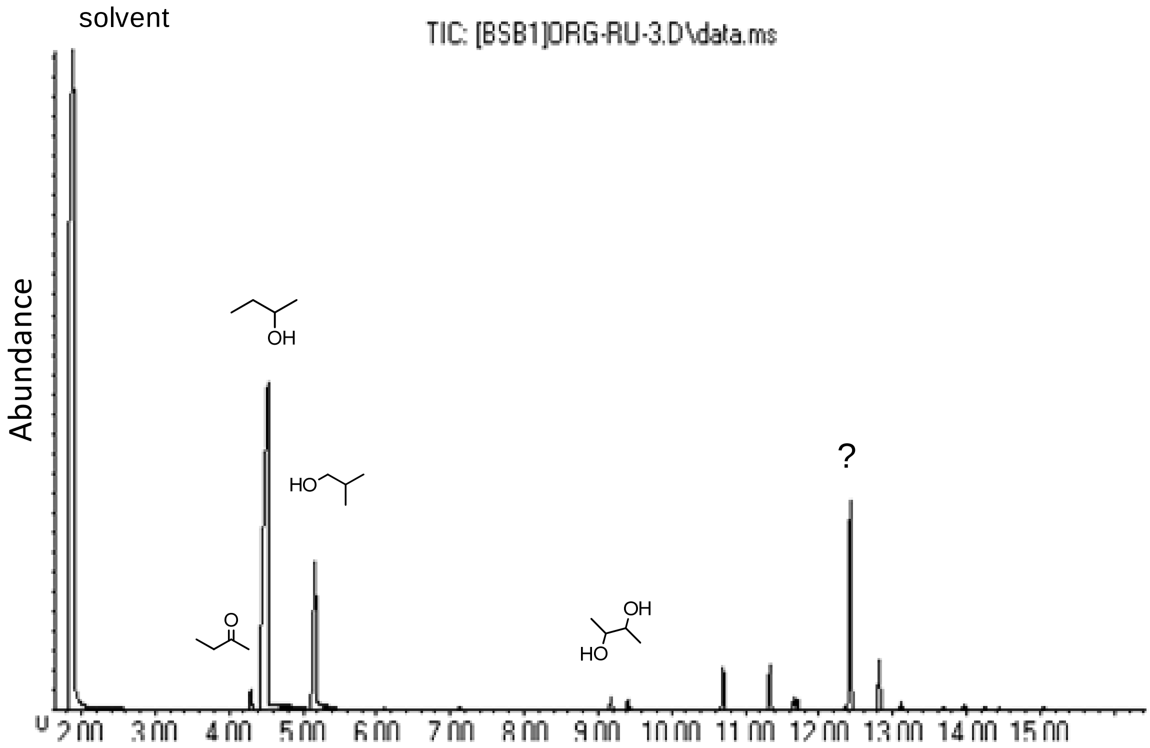


Figure 17. Reduction products using as feed the combined organic samples collected between 61.5 to 120.5 h in the conversion of LanzaTech BDO to MEK over H-ZSM-5(23).

3.3.4 Integrated Step-Wise Conversion of BDO to 2-Butanol

Above it was demonstrated that BDO can be converted to a product rich in MEK and that MEK can be converted to 2-butanol with a hydrogenation catalyst. Here, the results of testing with a combination of those two processes without intermediate separation are reported, demonstrating the direct conversion of BDO to 2-butanol in a flow reactor. The reactor consisted of two stages. In the first stage, feed BDO was converted to primarily MEK. The output of Stage 1 was fed directly to Stage 2, in which the MEK-rich product was hydrogenated to 2-butanol.

In the first stage, a tube was loaded with 2.79 g of H-ZSM-5 (23). The tube was heated to 300 °C for BDO dehydration. The tube comprising the second stage was loaded with 0.55 g of Ru/C (Engelhard) catalyst. The Ru/C catalyst was heated to 275 °C in H_2 (200 psig) for one hour to activate the catalyst prior to experimentation. (In retrospect, a longer activation time would have given better results.) The 2nd stage was heated to 160 °C during conversion experiments. LanzaTech BDO containing 10% water was used as the feed with a flow rate of 0.1 mL/min into the first stage. The H_2 flow rate was at 400 mL/min and the reactor pressure was 200 psig. The reactor performance was checked by sampling after each stage.

The first stage was tested with the H-ZSM-5(23) catalyst. Two samples were collected at the outlet of the first stage at the end of 2 and 3 hours. The analyses for organic and aqueous phases are listed below (Table 17) and GC traces are shown in Figure 18 and Figure 19. BDO was nearly completely converted to a mixture of primarily MEK and IBA.

Table 17. First stage product – conversion of BDO to MEK with H-ZSM-5 (23) catalyst

TOS (h)	T (°C)	BDO	MEK	IBA
2 (org)	300	0	44.9	6.4
2 (aq)	300	7.6	77.2	5.8
3 (org)	300		45	8.4
3 (aq)	300	1.3	74.5	7.4

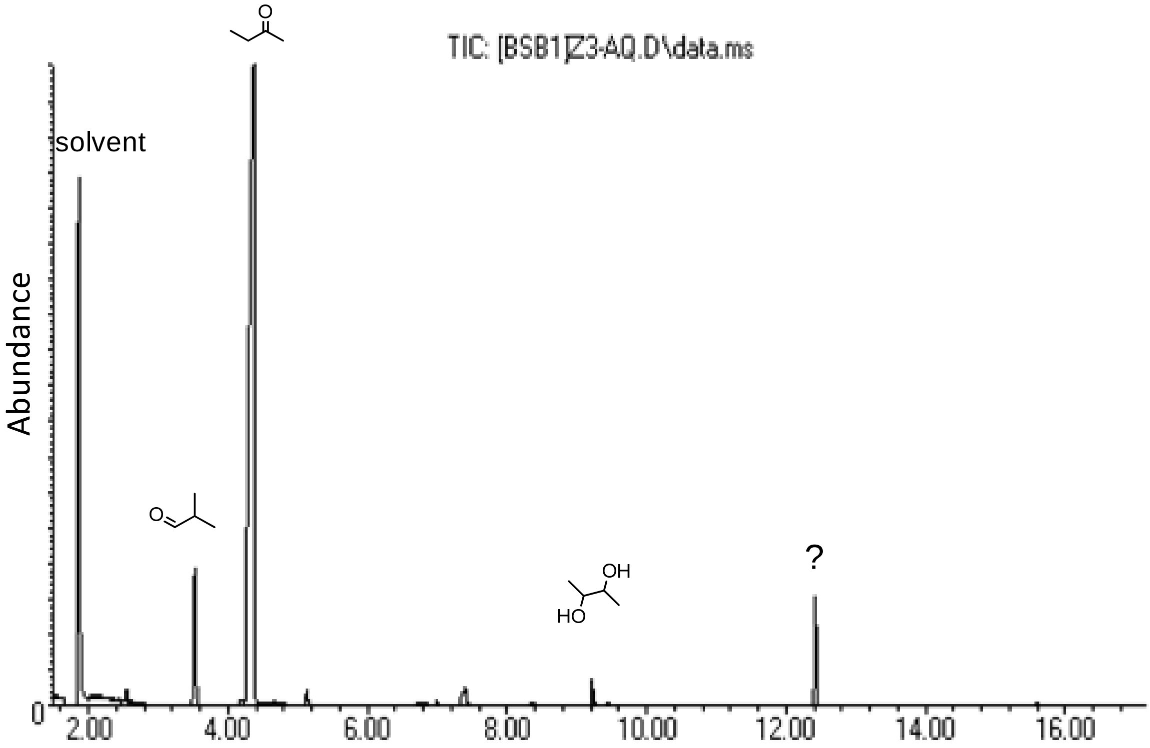


Figure 18. Aqueous phase sample taken at the outlet of the first stage of the combined reactor.

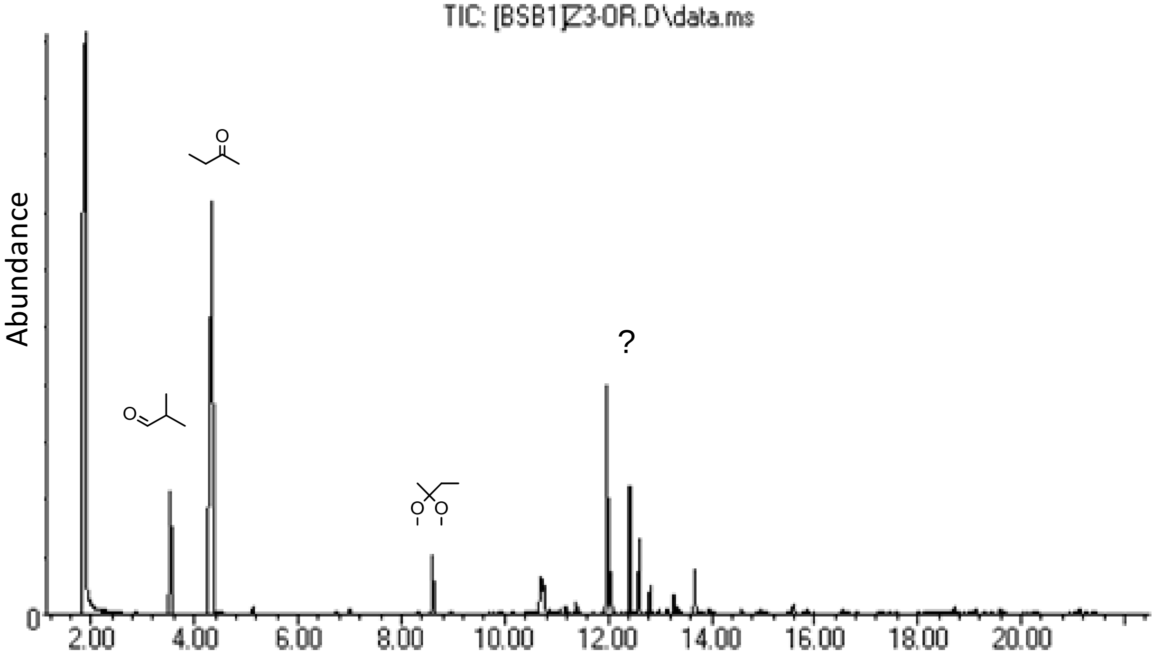


Figure 19. Organic phase sample taken at the outlet of the first stage of the combined reactor.

One sample was collected from the exit of the second stage after 2 hours and analyzed with GC/MS (Table 18, Figure 20, and Figure 21). IBA was completely converted to isobutanol and MEK was converted to 2-butanol in about 80% yield. Unconverted BDO remained primarily in the aqueous phase. Higher yields of 2-butanol should be attainable by more completely activating the Ru/C catalyst (or by using a different catalyst) and by adjusting the residence time in Stage 2. A higher overall conversion of BDO to 2-butanol could be attained by adjusting the residence time in Stage 1 as well. Such optimization would improve the performance of the reactor. Nevertheless, this experiment demonstrates the direct conversion of BDO to 2-butanol in high yield. A third stage could easily be added to convert the 2-butanol to fuels or butenes.

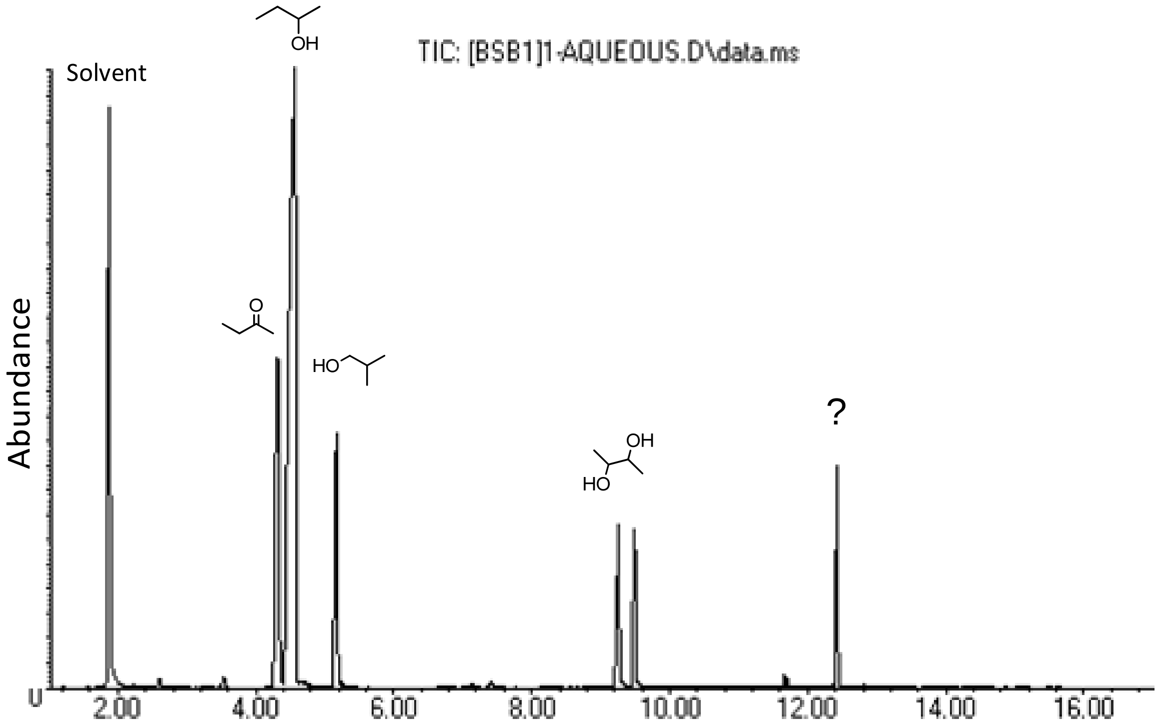


Figure 20. Aqueous phase sample taken at the outlet of the second stage of the combined reactor.

Table 18. Sample taken from the second stage of the combined two stage conversion of BDO to 2-butanol (1st stage: H-ZSM-5(23) run at 300 °C; 2nd stage: 5%Ru/C run at 160 °C)

Time (h)	MEK	IBA	2-Butanol	Isobutanol	BDO
2 (org)	10	0	47	6.9	0.52
2 (aq)	15.7	0	53.3	11.8	10.4

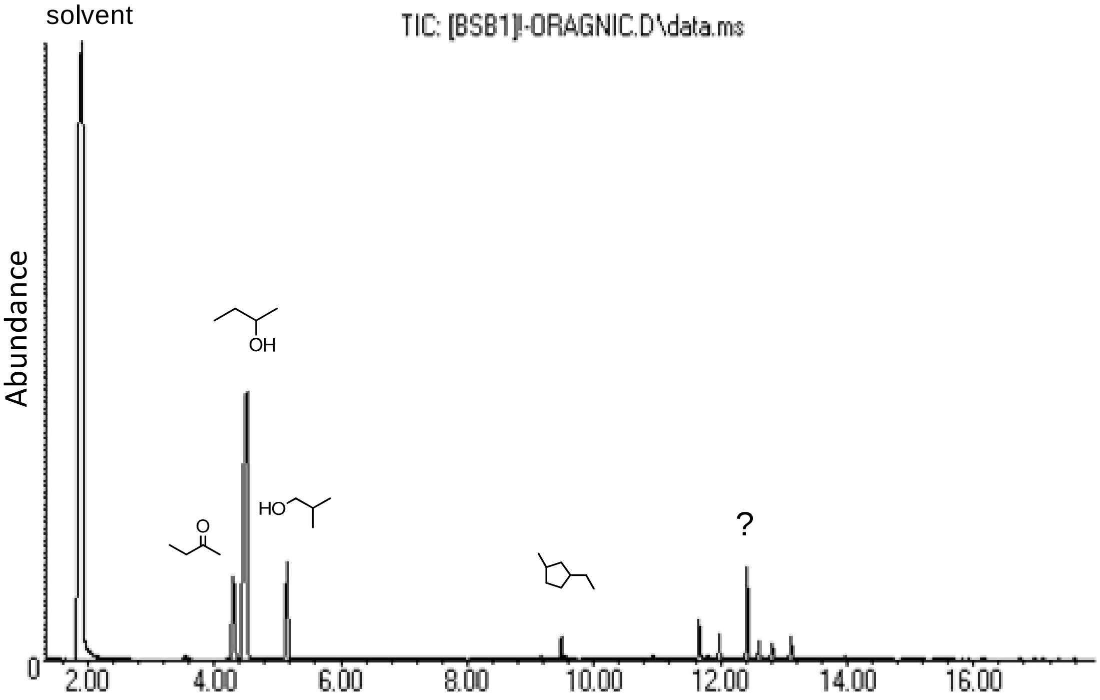


Figure 21. Organic phase sample taken at the outlet of the second stage of the combined reactor.

3.3.5 Conversion of 2-Butanol to Hydrocarbons

The conversion of 2-butanol to hydrocarbons was demonstrated over H-ZSM-5(30) catalyst at 400, 300, and 250 °C in the flow reactor. Typically, 1.2 g catalyst was used with a 2-butanol feed rate of 0.05 mL/min. The liquid product is a 2-phase mixture of hydrocarbons (top) and water (bottom) as shown in Figure 22.

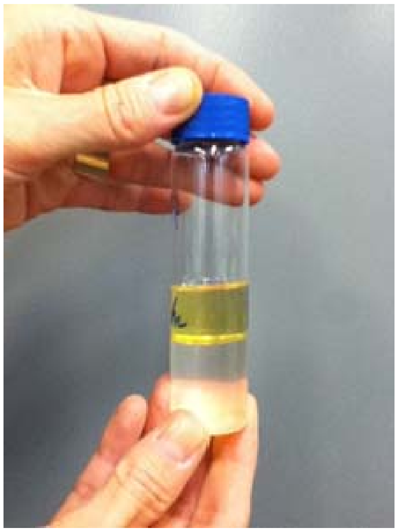


Figure 22. 2-phase liquid product formed by the conversion of 2-butanol over H-ZSM-5(30) catalyst.

Results obtained at 400 °C are shown in Table 19. Aromatics are formed at this temperature and the catalyst has a much longer lifetime (> 103 h) than when BDO or MEK were used as feeds (about 3 h). Performance appears to be very stable over the course of the experiment with no apparent deactivation. A typical GC trace is shown in Figure 23.

Table 19. Conversion of 2-butanol to hydrocarbons over H-ZSM-5(30)/Al_2O_3 catalyst at 400 °C

Conditions/ Selected Products	Sample # 1	2	3	5	11
Time (h)	3.2	5.2	15	24.7	103
T (°C)	400	400	400	400	450
MEK	6.3	1.1	0.4	0	0
Benzene	5.8	5.3	5.1	4.7	1.6
Toluene	11.2	11.5	11.4	11.3	7.1
Di-trimethyl-benzene	29.9	36	39.6	45	41.5

Decreasing the reactor temperature changed the product composition. At 300 °C the hydrocarbon fraction was made up of a mixture of aromatics and normal and branched olefins (Figure 24). Decreasing the temperature further to 250 °C gave a hydrocarbon product consisting of normal and branched C5 to >C12 olefins with almost no aromatic content (Figure 25). This fraction could be hydrotreated to provide a mixture of paraffins and isoparaffins as a blendstock for jet fuel.

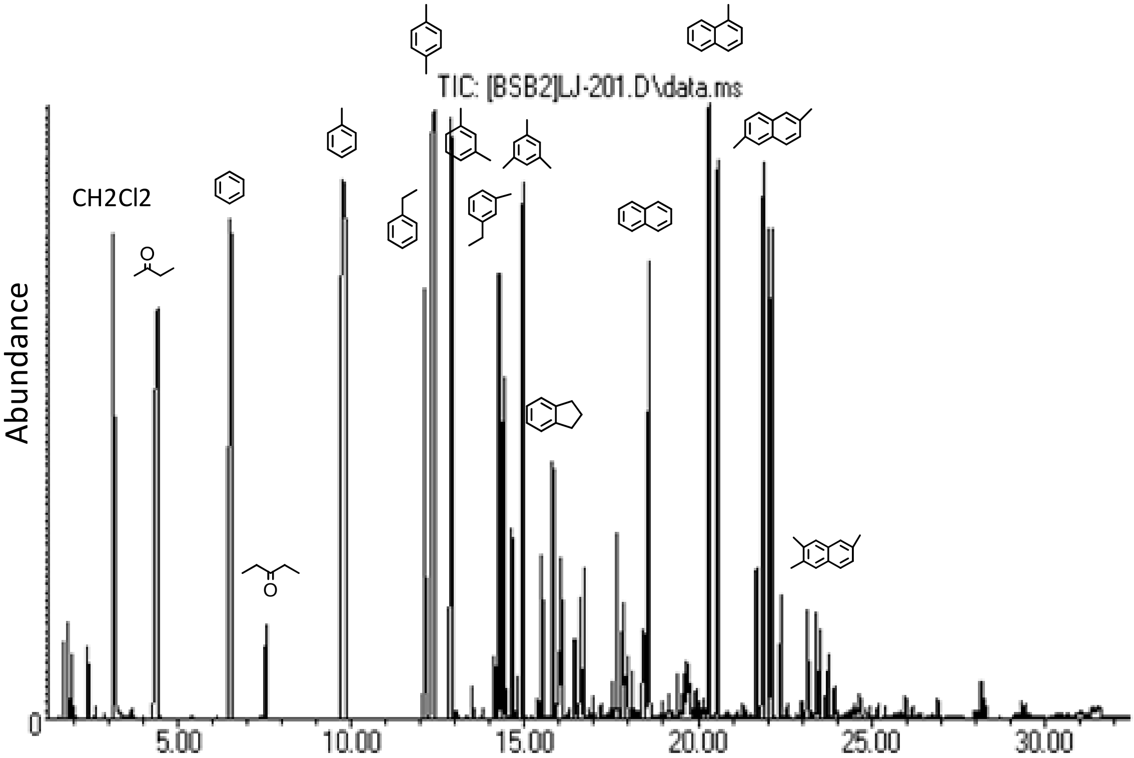


Figure 23. Conversion of 2-butanol to hydrocarbons over H-ZSM-5(30) at 400 °C

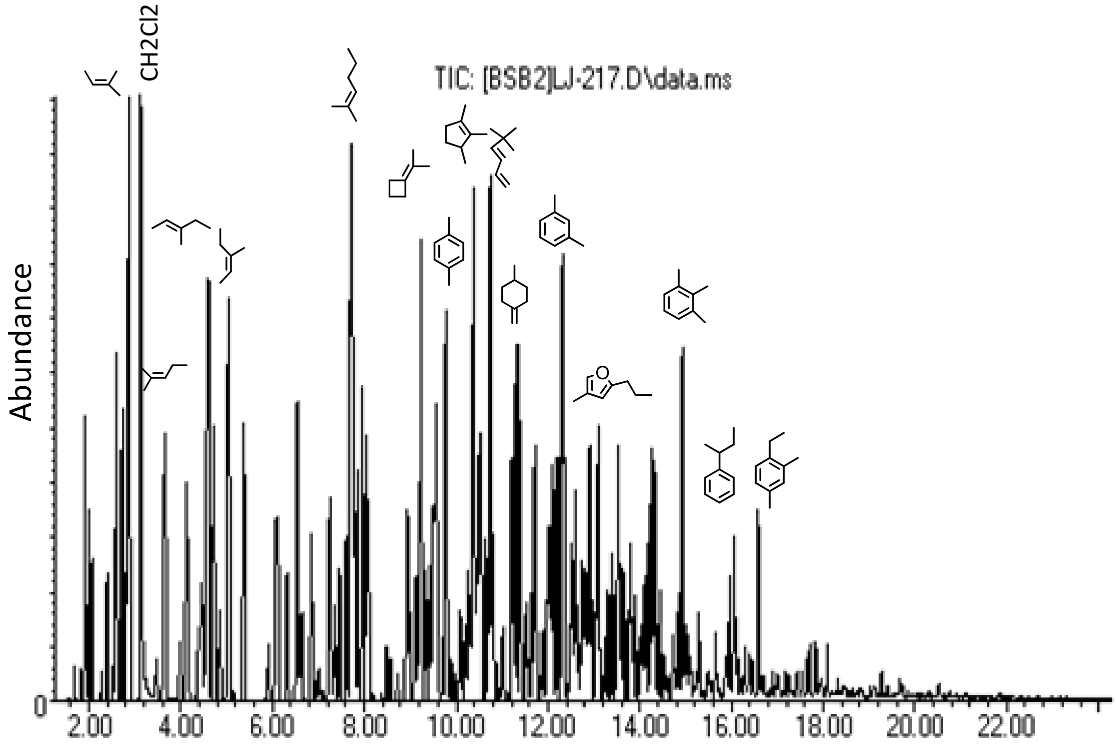


Figure 24. Conversion of 2-butanol to hydrocarbons over H-ZSM-5(30) at 300 °C

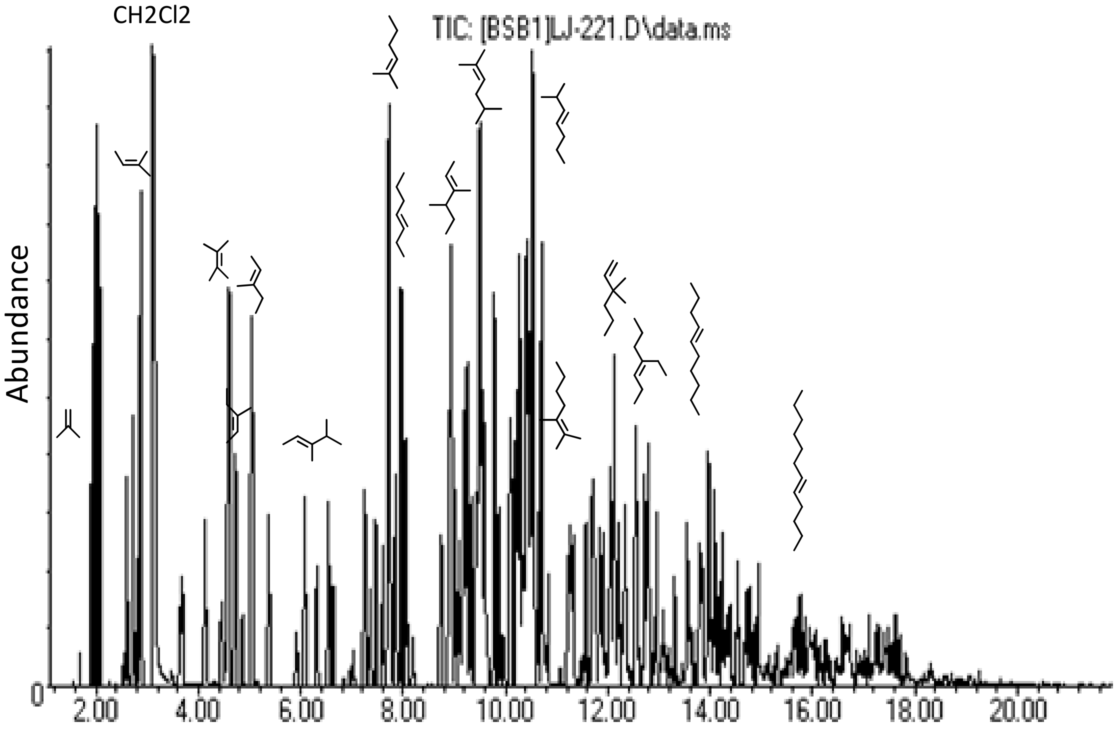


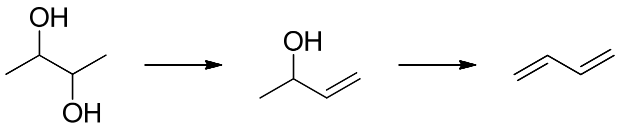
Figure 25. Conversion of 2-butanol to hydrocarbons over H-ZSM-5(30) at 250 °C.

3.4 Indirect BDO Conversion to Fuels Through Butadiene

Several methods for conversion of BDO to 1,3-butadiene (1,3BD) are known. Early work reported the esterification of BDO with acetic acid to the diacetate, followed by pyrolysis of the diacetate to 1,3-butadiene (Morell, 1945). The process was tested on the pilot scale (Schniepp, 1945). The per-pass yield of butadiene was 82% at temperatures of 575-600 °C. This approach is complicated by the corrosive nature of the acetic acid produced, which necessitates special materials of construction.

A secondary route to 1,3-butadiene starting with BDO is through 2-butenes, which are available either from 2-butanol by dehydration or from the 1,3-dioxolanes by acid catalyzed thermolysis. The butenes can be catalytically dehydrogenated to 1,3-butadiene in the presence of superheated steam as diluent and heating medium (Kearby, 1955).

Dehydration of 2,3-butandiol is another route to butadiene. However, over most catalysts the product is MEK. The only known catalyst for 1,3-butadiene is thoria (ThO_2), reported by M. E. Winfield (1945, 1950). The gas phase catalytic dehydration occurs between about 350 - 550°C and can achieve good yields of 1,3-butadiene with methyl vinyl carbinol as the major co-product. A combined methyl vinyl carbinol and butadiene yield up to about 87% was attained at 400°C under reduced (64 mm) pressure. Under these conditions, the (MVC+diene)/MEK ratio was about 9.



BDO MVC 1,3BD

Methyl vinyl carbinol is the initial dehydration product. Over thoria without water, the methyl vinyl carbinol can be dehydrated quickly to 1,3-butadiene at about 50 °C. However, in the presence of water, formed by the dehydration reaction, activity is retarded and conversion is incomplete. With dry reagents, thoria promotes MEK self condensation to methyl heptenone at room temperature. Butadiene oligomerizes on dried thoria.

While thorium oxide is the best single metal oxide catalyst described to date for conducting BDO dehydration to butadiene, it has the disadvantage of also being radioactive. Certain other metal oxides that are analogs to thoria, such as the rare-earth or rare-earth-like metal oxides, might also facilitate the desired transformation.

Lundeen (1963, 1967) reports numerous lanthanide, actinide, and early transition metal oxide catalysts for the selective dehydration of 2-alcohols to 1-olefins. Selectivities of the 1-olefins up to 97% at reaction temperatures ranging from 350 to 430 °C were reported. Whereas catalysts such as alumina promote *trans*- elimination leading to the more substituted 2-olefins (and in the case of BDO, further rearrangement of the enol to MEK), thoria analogs promote *cis*-elimination to the less substituted Hofmann products.

3.4.1 Summary of Pyroprobe Catalyst Screening for BDO to 1,3BD

This section presents a summary of catalyst screening results conducted in the pyroprobe apparatus. The complete listing of all of the catalysts tested and the results obtained are displayed at the end of Section 3.4 in Table 23. Conversion and product selectivity data were based on GC/MS area percents for BDO feedstock and of other products produced.

A single charge of the ALZ22 catalyst material, which was a La and Al doped ZrO_2 obtained from MEL Chemicals, was tested in 7 reruns in the pyroprobe apparatus. This catalyst maintained activity and selectivity, with BDO conversions over the series of runs ranging from 94% down to 50% and 1,3-butadiene selectivity as high as 65.7% and as low as 33.3%. Variability was not systematic and presumably represented experimental variation. This material still makes a fair amount of MEK, presumably from Brønsted sites on the catalyst, but did not produce MVC.

Table 20. Repeated conversion of BDO to 1,3BD with La + Al Doped ZrO_2 (ALZ22).

Run #	Notes	T (°C)	BDO % Conv.	1,3BD % Sel.	1,3BD % Yield	MEK % Sel.	MEK % Yield
1	Fresh Cat.	500	75.0	33.3	25.0	48.7	36.5
2	(1st Repeat)	500	93.5	65.7	61.4	26.5	24.8
3		500	94.0	56.5	53.1	27.8	26.1
4		500	50.0	41.0	20.5	46.2	23.1
5		500	92.0	50.4	46.4	37.3	34.3
6	60% flow	500	93.3	63.2	59.0	30.0	28.0
7	40% flow	500	53.0	64.9	34.4	65.1	34.5

A ranking of the nine best pyroprobe test results obtained from catalyst screening are shown in Table 21. Catalysts that produced 1,3BD and/or MVC were considered, since MVC should be relatively easily converted to 1,3BD. The catalyst designation, the optimum test temperature used, and the combined 1,3BD + MVC yield for that condition are given for each of the nine best catalyst/conditions tested.

Table 21. Best nine tests for 1,3BD and MVC production in pyroprobe screening experiments

Catalyst	Optimal T, °C	1,3BD+MVC % Yield
ALZ22	500	61.4
XZO691-01	500	58.0
Tm_2O_3	500	56.3
ALZ22	500	56.0
FZO2089	500	53.8
ALZ5C-4/D	500	48.7
ALZ22	500	42.7
FZO922	500	33.9
Sc_2O_3	700	31.7

As can be seen from the ranking, ALZ22 was involved in three of the top spots and FZO2089, a material equivalent to ALZ22, also performed well. The XZO691-01, the ALZ5C-4D, and the FZO922 catalysts (also MEL Chemicals products) ranked within the top nine spots and the Tm_2O_3 and Sc_2O_3, which were in-house prepared catalysts, also rose to the top.

3.4.2 Summary of Small Flow Reactor Testing

The small, packed-bed flow reactor was set up to validate results observed in pyroprobe testing. The catalyst chosen for flow testing was powdered FZO2089 because MEL Chemical, Inc. prepared it to be the equivalent to the ALZ22 product. The FZO2089 material is a proprietary mixed oxide preparation of aluminum, lanthanum, and zirconium. A portion of the powdered material was first pelletized, then ground and sieved to a 60-100 mesh size fraction that could be run in the flow reactor (our designation for the sieved FZO2089 material was 15095-32-3). This material had an apparent bulk density of 1.0924 g/cc and 0.5472 g (~0.5009 cc) was loaded into the reactor for testing.

A literature reference by Bhattacharyya (1963) described a fixed bed catalytic process for the conversion of ethanol to 1,3BD in about 55% yield. The process operated at atmospheric pressure at ~ 425^{o}C at a calculated contact time of about 1.95 seconds. Although the residence times for reactions run in the pyroprobe reactor were uncertain, the small flow reactor configuration was initially set up to mimic these literature conditions. The feedstock solution used for a majority of the runs was a 50 wt% solution of Aldrich BDO in deionized water.

A listing of the flow reactor runs using the 15095-32-3 catalyst is shown in Table 22. As can be seen, the highest 1,3BD yields were observed at the lowest reaction temperatures investigated near the end of the testing. It should be noted that a catalyst regeneration step was not implemented during the first 3 runs, but was shown to be important in subsequent runs.

BDO conversions were difficult to determine because mass balances in these experiments were poor. However, unconverted feed material was the predominant species present in most of the recovered liquids. Small amounts of dissolved 1,3BD were also observed in the recovered liquids (identified by GC/MS), usually accompanied by other butenes, but could not be easily quantified using the GC/MS method. These issues with quantification could be resolved in future work with improvements to the analytical methods used. Resources were not expended in this project to improve these methods because of the nature of the task as screening and the limited number of flow reactor tests that could be run.

The 1,3BD determinations were based entirely on gas phase analyses, which report moles of product. Therefore, yields were estimated as a percentage of total BDO fed. Because some 1,3BD was detected in the liquid phase which could not be quantified, the 1,3BD yields reported are considered to be conservative. Estimated yields were lower in the flow reactor than in the pyroprobe. Not enough experiments were run to make conclusions about this difference, but the amount of water in the feed is likely important and the degree of 1,3BD oligomerization on the catalyst is an important consideration.

At the completion of testing, catalyst burnout was not performed and the catalyst removed at that time was quite sticky, discolored, and had a strong odor. It is likely that a significant amount of oligomeric material was produced during the dehydration reaction that built up on the catalyst surface, contributing to the poor mass balances and decreased 1,3BD yields.

Future work would investigate the role of water in the feed. System pressure probably plays a role in efficient recovery of 1,3BD and minimization of follow-up reactions on the catalyst surface. Winfield conducted his experiments under a partial vacuum, so studies to determine the effects of pressure are advisable. Further catalyst testing of the other materials in Table 21 should also be conducted.

Table 22. Flow reactor results for the conversion of BDO to 1,3BD

Run #	Feed Composition	N_2 Gas Flow Rate, sccm	Liq. Feed Rate, mL/h	Contact Time, msec	T, °C	1,3 BD % Yield
60883-30	50% BDO	26.0	3	185	450	7.93
60883-33	50% BDO	50.5	3	126	500	3.49
60883-36	50% BDO	26.0	3	173	500	3.93
60883-39 *	50% BDO	26.0	3	173	500	5.74
60883-42 *	Neat BDO	51.4	3	189	450	3.77
60883-45 *	Neat BDO	50.6	3	206	400	8.82
60883-48 *	Neat BDO	101.6	3	114	400	8.33

* Catalyst regenerated by heating to 500 °C in air overnight prior to this run

Table 23. Summary of pyroprobe experiments for the conversion of BDO to 1,3BD (table continues on following pages).

Catalyst	Descriptor	Notes	T (°C)	BDO % Conv.	1,3BD % Sel.	1,3BD % Yield	MVC % Sel.	MVC % Yield	MEK % Sel.	MEK % Yield	Other % Sel.	Other % Yield
Silica Gel			300	10.0	0	0	0	0	0	0	100.0	10.0
Silica Gel			500	93.0	8.6	8.0	0	0	91.4	85.0	0	0
Alpha Alumina			300	10.0	0	0	0	0	0	0	100.0	10.0
Alpha Alumina			500	95.0	8.4	8.0	0	0	91.6	87.0	0	0
Pr-doped CeOx (deoxygenated)	15095-31-1		300	5.0	0	0	0	0	0	0	100.0	5.0
Pr-doped CeOx (deoxygenated)	15095-31-1		500	5.0	0	0	0	0	0	0	100.0	5.0
Pr-doped CeOx (deoxygenated)	15095-31-1		700	5.0	0	0	0	0	0	0	100.0	5.0
CeO2	60883-5-3		300	5.0	0	0	0	0	0	0	100.0	5.0
CeO2	60083-5-3		500	50.0	0	0	0	0	80.0	40.0	20.0	10.0
WO2.97	60883-5-1		300	65.0	0	0	0	0	76.9	50.0	23.1	15.0
WO2.97	60883-5-1		500	5.0	0	0	0	0	0	0	100.0	5.0
La2O3	60883-5-4		300	5.0	0	0	0	0	0	0	100.0	5.0
La2O3	60883-5-4		500	5.0	0	0	0	0	0	0	100.0	5.0
3 mole% Y-Stab. ZrO2	60883-5-2		300	5.0	0	0	0	0	0	0	100.0	5.0
3 mole% Y-Stab. ZrO2	60883-5-2		500	75.5	23.3	17.6	16.7	12.6	60.1	45.4	-0.1	-0.1
La + Al Doped ZrO2	ALZ22		300	10.0	0	0	0	0	0	0	100.0	10.0
La + Al Doped ZrO2	ALZ22		500	99.4	43.0	42.7	0	0	45.8	45.5	11.3	11.2
La + Al Doped ZrO2	ALZ22	(1st Repeat)	500	90.0	0	0	0	0	100.0	90.0	0	0
La + Al Doped ZrO2	ALZ22	(2nd Repeat)	500	90.0	16.4	14.8	0	0	66.7	60.0	16.9	15.2
Quartz Wool			?	79.0	9.2	7.3	0	0	62.2	49.1	28.6	22.6
La + Al Doped ZrO2	ALZ22	(Fresh Cat.)	500	75.0	33.3	25.0	0	0	48.7	36.5	18.0	13.5
La + Al Doped ZrO2	ALZ22	(1st Repeat)	500	93.5	65.7	61.4	0	0	26.5	24.8	7.8	7.3
La + Al Doped ZrO2	ALZ22	(2nd Repeat)	500	94.0	56.5	53.1	0	0	27.8	26.1	15.7	14.8
La + Al Doped ZrO2	ALZ22	(3rd Repeat)	500	50.0	41.0	20.5	0	0	46.2	23.1	12.8	6.4
La + Al Doped ZrO2	ALZ22	(4th Repeat)	500	92.0	50.4	46.4	0	0	37.3	34.3	12.3	11.3

Catalyst	Descriptor	Notes	T (°C)	BDO % Conv.	1,3BD % Sel.	1,3BD % Yield	MVC % Sel.	MVC % Yield	MEK % Sel.	MEK % Yield	Other % Sel.	Other % Yield
La + Al Doped ZrO2	ALZ22	(5th R.R., 60%Flow)	500	93.3	63.2	59.0	0	0	30.0	28.0	6.8	6.3
La + Al Doped ZrO2	ALZ22	(6th R.R., 40%Flow)	500	53.0	64.9	34.4	0	0	65.1	34.5	-30.0	-15.9
3 mole% Y-Stab. ZrO2	60883-5-2		500	38.0	21.1	8.0	10.8	4.1	41.6	15.8	26.6	10.1
3 mole% Y-Stab. ZrO2	60883-5-2		500	38.0	23.7	9.0	14.5	5.5	42.9	16.3	18.9	7.2
5% PMA on TiO2	60883-12-1		250	53.0	0	0	0	0	64.2	34.0	35.8	19.0
5% PMA on TiO2	60883-12-1		350	50.0	0	0	0	0	58.0	29.0	42.0	21.0
Sm2O3	60883-11-2		300	61.5	0	0	0	0	65.0	40.0	35.0	21.5
Sm2O3	60883-11-2		500	55.0	9.6	5.3	0	0	75.1	41.3	15.3	8.4
Sm2O3	60883-11-2		700	74.5	19.7	14.7	0	0	53.7	40.0	26.6	19.8
Yb2O3	60883-11-1		500	65.0	20.8	13.5	0	0	38.5	25.0	40.8	26.5
Yb2O3	60883-11-1		700	60.0	2.7	1.6	0	0	59.7	35.8	37.7	22.6
Gd2O3	60883-13-3		500	46.0	0	0	0	0	45.7	21.0	54.3	25.0
Ho2O3	60883-9-2		500	45.7	14.7	6.7	0	0	58.0	26.5	27.4	12.5
Ho2O3	60883-9-2		700	57.5	7.9	4.6	0	0	56.7	32.6	35.4	20.3
Eu2O3	60883-13-1		500	30.0	6.7	2.0	0	0	60.0	18.0	33.3	10.0
Eu2O3	60883-13-1		700	66.0	14.5	9.6	5.0	3.3	50.0	33.0	30.5	20.1
Dy2O3	60883-13-2		500	49.0	0	0	0	0	61.2	30.0	38.8	19.0
Dy2O3	60883-13-2		700	63.4	8.2	5.2	0	0	63.1	40.0	28.7	18.2
Zr(OH)4-Ca(OH)2	XZO 691-01		300	44.0	0	0	0	0	54.5	24.0	45.5	20.0
Zr(OH)4-Ca(OH)2	XZO 691-01		500	97.5	59.5	58.0	0	0	24.6	24.0	15.9	15.5
Zr(OH)4-Ca(OH)2	XZO 691-01		700	84.0	28.5	23.9	0	0	38.1	32.0	33.5	28.1
Zr(OH)4-Ca(OH)2	XZO 691-01	(1st Repeat)	500	96.4	44.6	43.0	0	0	27.0	26.0	28.4	27.4
Zr(OH)4-Ca(OH)2	XZO 691-01	(2nd Repeat)	500	66.4	30.1	20.0	0	0	39.2	26.0	30.7	20.4
Zr(OH)4-Ca(OH)2	XZO 691-01	(3rd Repeat)	500	55.0	6.4	3.5	0	0	61.8	34.0	31.8	17.5
Calcined Zr(OH)4-Ca(OH)2 (900C)	60883-14-1		500	73.3	27.3	20.0	7.5	5.5	47.7	35.0	17.5	12.8
Calcined Zr(OH)4-Ca(OH)2 (900C)	60883-14-1	(1st Repeat)	500	49.9	21.4	10.7	0	0	49.1	24.5	29.5	14.7
Al-Doped ZrO2	ALZ5C-4/D		500	100.0	48.7	48.7	0	0	28.6	28.6	22.7	22.7

Catalyst	Descriptor	Notes	T (°C)	BDO % Conv.	1,3BD % Sel.	1,3BD % Yield	MVC % Sel.	MVC % Yield	MEK % Sel.	MEK % Yield	Other % Sel.	Other % Yield
Al-Doped ZrO2	ALZ5C-4/D		500	74.0	34.7	25.7	0	0	33.8	25.0	31.5	23.3
Zr(OH)4	FZO922		500	100.0	33.9	33.9	0	0	20.0	20.0	46.1	46.1
Zr(OH)4	FZO922		700	83.5	35.9	30.0	0	0	49.1	41.0	15.0	12.5
Ce-Doped ZrO2	802		500	50.4	26.8	13.5	0	0	48.2	24.3	25.0	12.6
Ce-Doped ZrO2	802		700	88.0	13.3	11.7	0	0	46.6	41.0	40.1	35.3
Calcined ALZ22 (900C)	60883-15-1		500	69.0	25.4	17.5	0	0	46.8	32.3	27.8	19.2
Calcined ALZ22 (900C)	60883-15-1	(1st Repeat)	500	53.0	28.7	15.2	0	0	47.2	25.0	24.2	12.8
Calcined ALZ22 (900C)	60883-15-1	(2nd Repeat)	500	63.0	21.7	13.7	0	0	50.0	31.5	28.3	17.8
8mole% Y-Stab. ZrO2	60883-3-2		300	0	0	0	0	0	0	0	0	0
8mole% Y-Stab. ZrO2	60883-3-2		500	38.0	0	0	0	0	56.8	21.6	43.2	16.4
10mole% Y-Stab. ZrO2	60883-3-3		300	0	0	0	0	0	0	0	0	0
10mole% Y-Stab. ZrO2	60883-3-3		500	28.0	10.0	2.8	0	0	50.7	14.2	39.3	11.0
13mole% Y-Stab. ZrO2	60883-3-4		300	0	0	0	0	0	0	0	0	0
13mole% Y-Stab. ZrO2	60883-3-4		500	38.0	0	0	0	0	16.6	6.3	83.4	31.7
La + Al Doped ZrO2	ALZ22		500	88.0	63.6	56.0	31.0	27.3	0	0	5.3	4.7
Ho2O3	60883-6-1		300	11.0	0	0	0	0	0	0	100.0	11.0
Ho2O3	60883-6-1		500	7.0	0	0	0	0	0	0	100.0	7.0
Ho2O3	60883-6-1		700	40.0	0	0	0	0	60.8	24.3	39.3	15.7
Y2O3	60883-6-2		300	0	0	0	0	0	0	0	0	0
Y2O3	60883-6-2		500	0	0	0	0	0	0	0	0	0
3mole% Y-Stab. ZrO2	60883-5-2		500	38.0	23.7	9.0	14.5	5.5	42.9	16.3	18.9	7.2
3mole% Y-Stab. ZrO2	60883-5-2		500	37.1	21.0	7.8	11.1	4.1	42.6	15.8	25.3	9.4
Y2O3	60883-6-2		300	1.0	0	0	0	0	0	0	100.0	1.0
Y2O3	60883-6-2		500	6.0	0	0	0	0	0	0	100.0	6.0
La2O3	60883-7-1		500	8.0	0	0	0	0	0	0	100.0	8.0
La2O3	60883-7-1		700	23.2	0	0	0	0	53.0	12.3	47.0	10.9
Nd2O3	60883-7-2		500	5.0	0	0	0	0	0	0	100.0	5.0

Catalyst	Descriptor	Notes	T (°C)	BDO % Conv.	1,3BD % Sel.	1,3BD % Yield	MVC % Sel.	MVC % Yield	MEK % Sel.	MEK % Yield	Other % Sel.	Other % Yield
Nd2O3	60883-7-2		700	33.0	20.6	6.8	10.3	3.4	48.5	16.0	20.6	6.8
Ho2O3	60883-9-2		500	6.0	0	0	0	0	0	0	100.0	6.0
Ho2O3	60883-9-2		700	40.0	0	0	0	0	78.3	31.3	21.8	8.7
Er2O3	60883-10-1		300	1.0	0	0	0	0	0	0	100.0	1.0
Er2O3	60883-10-1		500	13.0	30.8	4.0	0	0	31.5	4.1	37.7	4.9
Er2O3	60883-10-1		700	42.0	22.1	9.3	5.7	2.4	61.4	25.8	10.7	4.5
Tm2O3	60883-9-1		300	1.0	0	0	0	0	0	0	100.0	1.0
Tm2O3	60883-9-1		500	91.5	61.5	56.3	0	0	26.3	24.1	12.1	11.1
Tm2O3	60883-9-1		700	89.0	28.2	25.1	0	0	28.5	25.4	43.3	38.5
Tb4O7	60883-17-1		300	30.0	0	0	0	0	0	0	100.0	30.0
Tb4O7	60883-17-1		500	48.0	0	0	0	0	18.1	8.7	81.9	0
Tb4O7	60883-17-1		700	64.0	0	0	0	0	20.5	13.1	79.5	50.9
Lu2O3	60883-19-1		300	4.0	0	0	0	0	0	0	100.0	4.0
Lu2O3	60883-19-1		500	32.5	30.8	10.0	0	0	36.9	12.0	32.3	10.5
Lu2O3	60883-19-1		700	85.7	20.1	17.2	6.2	5.3	22.2	19.0	51.6	44.2
Sc2O3	60883-19-2		300	7.0	0	0	0	0	71.4	5.0	28.6	2.0
Sc2O3	60883-19-2		500	45.4	30.2	13.7	11.2	5.1	33.0	15.0	25.6	11.6
Sc2O3	60883-19-2		700	75.3	29.2	22.0	12.9	9.7	27.0	20.3	30.9	23.3
HfO2	60883-21-1		300	4.0	0	0	0	0	0	0	100.0	4.0
HfO2	60883-21-1		500	31.5	27.6	8.7	0	0	38.7	12.2	33.7	10.6
HfO2	60883-21-1		700	40.0	0	0	0	0	78.3	31.3	21.8	8.7
Pr6O11	60883-18-1		300	4.0	0	0	0	0	0	0	100.0	4.0
Pr6O11	60883-18-1		500	73.0	0	0	0	0	11.0	8.0	89.0	65.0
Pr6O11	60883-18-1		700	68.0	0	0	0	0	17.1	11.6	82.9	56.4
50mole%ZnO/50mole%SiO2	60883-22-1		500	23.9	11.3	2.7	0	0	68.2	16.3	20.5	4.9
50mole%ZnO/50mole%SiO2	60883-22-1		700	40.5	15.3	6.2	0	0	60.0	24.3	24.7	10.0
H.P. HfO2 powder			500	24.7	12.2	3.0	5.3	1.3	60.0	14.8	22.6	5.6

Catalyst	Descriptor	Notes	T (°C)	BDO % Conv.	1,3BD % Sel.	1,3BD % Yield	MVC % Sel.	MVC % Yield	MEK % Sel.	MEK % Yield	Other % Sel.	Other % Yield
H.P. HfO2 powder			700	67.5	9.8	6.6	4.7	3.2	60.0	40.5	25.5	17.2
3mole% Sc Stabilized ZrO2	Praxair		500	14.7	10.2	1.5	3.4	0.5	58.6	8.6	27.8	4.1
3mole% Sc Stabilized ZrO2	Praxair		700	68.5	14.6	10.0	1.9	1.3	57.2	39.2	26.3	18.0
10wt% Tm2O3 on Aerosil 380	60885-102-1		500	65.8	11.6	7.6	0	0	62.6	41.2	25.8	17.0
10wt% Tm2O3 on Aerosil 380	60885-102-1		700	79.4	13.4	10.6	0	0	61.5	48.8	25.2	20.0
Ta2O5 -325 mesh pdr.			500	17.8	10.1	0	0	0	58.4	0	31.5	5.6
La + Al Doped ZrO2	ALZ22		500	94.8	57.0	54.0	0	0	32.1	30.4	11.0	10.4
La + Al Doped ZrO2	ALZ22		700	100.0	0	0	0	0	0	0	100.0	100.0
La + Al Doped ZrO2	FZO2089	ALZ22 Equivalent	500	84.0	56.0	47.0	0	0	30.4	25.5	13.7	11.5
La + Al Doped ZrO2	FZO2089	ALZ22 Equivalent	700	89.8	24.5	22.0	0	0	55.7	50.0	19.8	17.8
Calcined FZO2089 (550C)	15095-32-2		500	92.5	51.9	48.0	0	0	25.4	23.5	22.7	21.0
Calcined FZO2089 (550C)	15095-32-2		700	87.1	47.1	41.0	0	0	36.2	31.5	16.8	14.6
Calcined FZO2089 (650C)	15095-32-3		500	92.9	57.9	53.8	0	0	23.1	21.5	18.9	17.6
Calcined FZO2089 (650C)	15095-32-3		700	87.4	47.3	41.3	0	0	34.3	30.0	18.4	16.1
Boron Oxide Glass			500	56.9	5.3	3.0	0	0	101.9	58.0	-7.2	-4.1

3.5 Techno-Economic and Life-Cycle Analyses

Techno-economic and life cycle analyses were conducted for parallel conversion of ethanol and BDO to a jet fuel blend. The potential to produce butadiene as a chemical product was also determined.

3.5.1 Conversion to Jet Fuel Blendstock

The process has four main processing areas: gasification and syngas conditioning, fermentation, oxygenate conversion to fuels and/or products and steam generation, as shown in the block flow diagram (Figure 26). Currently, ethanol and BDO are obtained as separate streams from the fermentation broth. Separate conversion is assumed, followed by combination to the final blendstock.

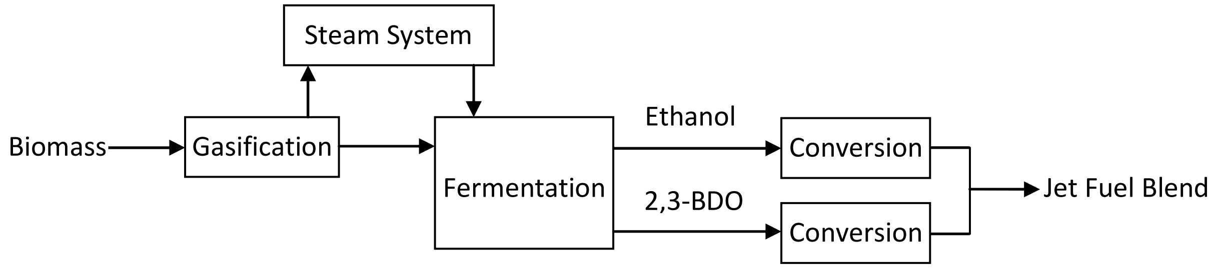


Figure 26. Process block flow diagram

The modeling and economic assumptions are similar to those used in the Office of Biomass Programs (OBP) design cases (Dutta, 2011): 2000 mtpd wood, an indirectly heated gasifier, and waste heat usage for electricity generation. The economic assumptions are nth plant, 2007 USD, 10% IRR, 96% stream factor and Modified Accelerated Cost Recovery System (MACRS) depreciation. Table 24 shows how the production cost of jet changes as a function of the feedstock cost, the capital cost of the conversion plant, and yield of ethanol and BDO to jet fuel.

Given these assumptions, it appears that the estimated production costs are between \$3 and \$4/gallon of jet blendstock. It must be stressed that these costs are preliminary, that they have not been optimized for full integration across the entire process, and that assumptions have not been validated experimentally.

Table 24. Dependence of jet fuel blendstock production cost as a function of feedstock costs, capital costs of the conversion plant, and yields of ethanol and BDO to jet fuel

	Ethanol to BDO ratio = 0.001/1							
% Conversion to liquid fuels	100				80			
Feedstock Cost, $/ton	$60		$80		$60		$80	
Oxygenate to Jet Capex MM$	50	75	50	75	50	75	50	75
Jet fuel cost, $/gal	$2.90	$3.00	$3.30	$3.40	$3.50	$3.60	$3.90	$4.00
	Ethanol to BDO ratio = 10/1							
% Conversion to liquid fuels	100				80			
Feedstock Cost, $/ton	$60		$80		$60		$80	
Oxygenate to Jet Capex MM$	50	75	50	75	50	75	50	75
Jet fuel cost, $/gal	$3.30	$3.50	$3.70	$3.90	$3.70	$3.80	$4.20	$4.30

In the process studied, the ethanol/BDO ratio has an impact on the fuel blend cost; higher concentrations of BDO from the fermentor help to reduce costs. The ratios chosen for the analysis bracket the possible range. A ratio of 3:1 has been demonstrated and significantly higher concentrations of BDO are considered technically feasible with further bioprocess development. In the conversion to fuels step, the longer-chain BDO-derived intermediates have advantages over ethanol for fuel production as they are more easily converted to isoparaffins. Therefore, there is both an economic and technical benefit to improving the fermentation process to give higher yields of BDO.

An additional sensitivity considered the trade-off between using a tar cracker versus a tar reformer. The results from the tar cracker case are presented in the above table. The tar reformer case has a higher yield, but also higher capital and operating costs and overall did not appear to improve the economics over the tar cracker case. The higher yield is a result of reforming the methane in the syngas to additional hydrogen and carbon monoxide plus a higher H_2/CO ratio to the fermentor. However, tar reformers are more expensive than tar crackers and the offgas from the fermentor has a very low BTU value requiring supplemental natural gas to make the offgas combustible. In the tar cracker case, the syngas methane passes through the fermentor to the offgas resulting in a medium BTU gas that can be used as fuel gas for steam production.

Stream factor proved to be an important parameter. Decreasing the stream factor significantly increased costs. Therefore, it is important to develop processes and catalysts that do not deactivate and result in down-time. This suggests that, for example, feeding BDO or MEK to the fuel conversion reactor, whether neat or in combination with other feed materials, should be avoided since they will lead to coking and catalyst deactivation. Rather, conversion of these compounds to intermediates such as 2-butanol, butadiene, or MEK oligomers is an important strategy for maximizing process longevity.

3.5.2 Product Opportunities

Further sensitivity analysis aids in understanding the potential for chemical by-products (for example, BDO or butadiene) as a way to improve the economics of an integrated biorefinery. A cursory analysis of the co-production of ethanol and BDO in a 5/1 ratio, then converting BDO to butadiene suggests favorable economics. For a production cost for ethanol of $2/gal, a butadiene price of $1/lb is estimated. The average market value of butadiene is $1/lb, so butadiene appears to be a viable product worthy of future examination.

3.5.3 Greenhouse Gas Analysis

Greenhouse gas (GHG) emissions are estimated for the jet fuel blend produced from the BDO process and compared to previously established estimates for petroleum derived jet fuel (Skone, 2008). This is a very high-level scoping analysis, the goal being to provide an initial estimate of GHG reductions associated with this pathway relative to petroleum-derived jet fuel and to help identify the major drivers affecting GHGs for the fuel production plant. The primary life cycle stages included in this analysis are feedstock production/collection, fuel production and fuel combustion in an aircraft (i.e., “field-to-wheels”), as illustrated in Figure 27. Indirect effects, such as indirect land use change, are not included in this preliminary analysis.

The life cycle of jet fuel is modeled in SimaPro using mass and energy balance data from the ChemCad process models and previous inventory estimates for stages other than biomass conversion (Hsu, 2011; Hsu et al, 2010; Hsu, personal communication). The process model used for this analysis is a 1:10 EtOH:BDO ratio and yields a jet fuel blend with an energy content (Lower Heating Value) of 20.1 MJ/lb (1.903×10^4 Btu/lb). The biomass feedstock is assumed to be forest residue, the waste product remaining after tree harvesting. Life cycle inventories for secondary materials and energy are taken

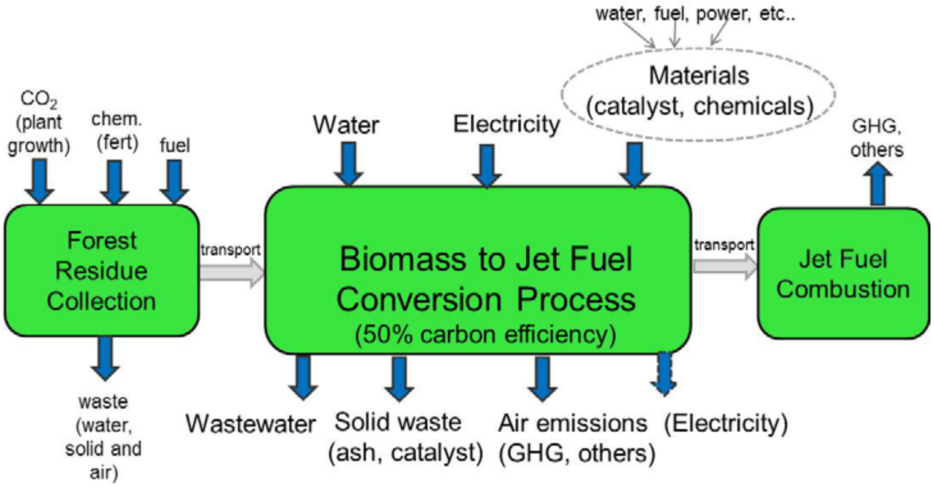


Figure 27. General life cycle of biomass-based jet fuel

Table 25. IPCC 2007 global warming potentials of the primary greenhouse gases for fuel production

Compound	Abbreviation	GWP, CO_2-equivalents
Carbon dioxide	CO_2	1
Methane	CH_4	25
Nitrous oxide	N_2O	298

from the Ecoinvent database (Ecoinvent, 2009). Calculation of greenhouse gases in CO_2-equivalents (CO_2-e) is based on the International Panel on Climate Change (IPCC) 100-year global warming potentials, shown in Table 25 (Solomon, 2007). The functional unit used for this study is 1 MJ of fuel combusted in an aircraft.

The life cycle GHG emissions for bio-based jet fuel and petroleum-based jet fuel, along with the relative contribution of each stage (see Figure 27) are shown in **Figure 28**. Bio-based jet fuel emissions are 1.6 g CO_2-e/MJ fuel, a reduction of 98% from petroleum-based jet fuel at 88.1 g CO_2-e/MJ (Skone, 2008). The primary reason for this large reduction in emissions is that the conversion process is producing power, which is assumed to be exported to the grid, effectively counting as an emissions credit (negative carbon emissions) due to the displacement of fossil power production (assumed average U.S. grid mix). Note also that the Fuel Use component in Figure 28 for the bio-based jet fuel is zero because biomass is considered a carbon-neutral feedstock. In other words, the CO_2 that is emitted during fuel combustion

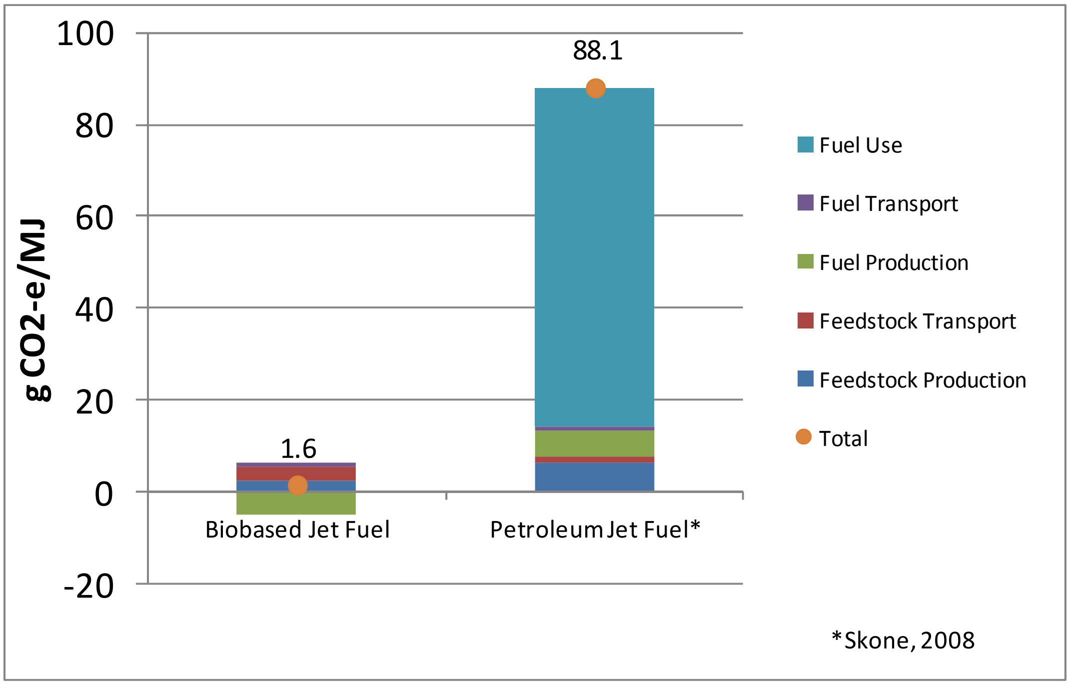


Figure 28. The life cycle GHG emissions for bio-based jet fuel and petroleum-based jet fuel

is essentially equal to that taken up from the atmosphere during plant growth, and therefore, only fossil carbon is accounted for in the analysis. This currently is a generally accepted method of carbon accounting for bio-based fuels. The small amount of biogenic methane produced during fuel combustion has been ignored for the purposes of this preliminary analysis.

The largest contributors to GHG emissions for biofuels are generally direct fossil fuel inputs (e.g., supplementary fuel for hydrogen production) and fossil-based power consumption (e.g., grid power). Because this process requires no supplementary fuel gas and produces power, it is showing very low GHG emissions relative to petroleum fuel. To illustrate the relationship between power and GHGs, a quick sensitivity was performed varying the net power for the conversion plant, the results of which are shown in Table 26.

It should be emphasized that these results are very preliminary and various data gaps exist at this stage in the model development. For example, data quantifying the methane product from anaerobic digestion of sludge from fermentation was not available. Additional methane from this process can be

Table 26. Dependency of GHG calculation on power balance for the 10:1 BDO:EtOH conversion plant

Net Power for Conversion Plant, MW	GHG Emissions, CO_2-e/MJ	Reduction from Petroleum Jet Fuel (Skone, 2008)*
4.3	1.6	98%
0	6.8	92%
-4.3	12	86%
-23	34	61%

*NETL (Skone, 2008) baseline value for petroleum jet is 88 g CO_2-e/MJ fuel.

fed to the steam boiler, resulting in increased power output and thus decreased GHG results for the pathway. Energy and materials inventory data for the fermentation inoculum feed was not included in the life cycle inventory. Also, the inventory for the tar cracker/reformer catalyst was estimated using a zeolite manufacturing process as a proxy, and catalyst consumption for the BDO and ethanol conversion reactors (dehydration, oligomerization, hydrogenation) is not known at this time. Although catalyst is likely not a large contributor to GHGs compared to direct fossil power and fuel inputs, other aspects of sustainability may be pertinent (e.g., soil, groundwater and resource depletion effects from mining). As more detailed process data become available, the SimaPro model for this pathway can be updated and more in-depth LCAs can be performed.

3.6 Subject Inventions Derived Under the CRADA

Three invention reports were filed as a result of this work and disclosed to LanzaTech, Inc.:

- 30024-E, “2,3-Butanediol Recovery Using Boron Reagents”, filed August 15, 2011, disclosed August 16, 2011
- 30109-E, “Conversion of 2,3-Butanediol to Butadiene”, filed January 17, 2012, disclosed January 31, 2012
- 30110-E, “Conversion of BDO to 2-Butanol and Fuels”, filed January 17, 2012, disclosed January 31, 2012

4 Conclusions and Recommendations

Several direct and indirect pathways from BDO to fuels were investigated in this project. Direct conversion of BDO over zeolitic solid acid catalysts produces aromatics, but catalyst lifetimes are too short to be industrially practical. MEK as a feed gave the same results as BDO, likely a result of MEK being an intermediate in BDO conversion.

Much better results were obtained by the indirect conversion to fuels through 2-butanol as an intermediate. In this process, BDO is initially dehydrated to MEK, which is then hydrogenated to 2-butanol. These two processes were successfully integrated into a single unit operation allowing 90% aqueous BDO to be converted to 2-butanol in high yield. 2-Butanol was separately converted over H-ZSM-5 to either aromatics or to linear and branched olefins depending on processing temperature. At 400 °C, aromatics were produced without loss of catalyst activity for over 5 days. C5 to >C12 olefins were produced at 250 °C and a mixture of aromatics and olefins were produced at 300 °C. Hydrotreating the olefin products would provide a jet-range blendstock of linear and isoparaffins. The BDO to 2-butanol process could easily be further integrated with either a fuel-forming step or with a dehydration step to produce butenes as chemical products.

Preliminary testing has identified several potentially viable catalysts for the conversion of BDO to 1,3-butadiene. The best catalysts are analogs of thoria, the only previously known catalyst for this transformation, and comprise early transition metal or lanthanide oxides. Some of these materials are commercially available. One catalyst material tested maintained activity and selectivity over 7 reruns in the pyroprobe apparatus. BDO conversions over the series of runs ranged from 94% down to 49.1% with 1,3-butadiene selectivity as high as 65.7% and as low as 33.3%. Limited flow reactor testing verifies activity for butadiene formation, but further testing is needed to attain conversions and selectivities observed in small scale catalyst screening.

The TEA analysis indicated that cost-competitive biorenewable hydrocarbon fuels from biomass are within reach given the assumptions made. Given these assumptions, it appears that the estimated production costs are between $3 and $4/gallon of jet blendstock. These costs are preliminary, they have not been optimized for full integration across the entire process, and assumptions have not been validated experimentally.

The life cycle GHG emissions for bio-based jet fuel and petroleum-based jet fuel, along with the relative contribution of each stage were determined. Bio-based jet fuel emissions are 1.6 g CO_2-e/MJ fuel, a reduction of 98% from petroleum-based jet fuel at 88.1 g CO_2-e/MJ. The primary reason for this large reduction in emissions is that the conversion process produces power, which is assumed to be exported to the grid, effectively counting as an emissions credit (negative carbon emissions) due to the displacement of fossil power production (assumed average U.S. grid mix). Because biomass is considered a carbon-neutral feedstock, the amount of carbon that is emitted during fuel combustion is the same as that taken up from the atmosphere during plant growth, and therefore, only fossil carbon is accounted for in the analysis.

The results of the TEA analysis are significant because the overall process of gasification of biomass, fermentive conversion of syngas to oxygenate products, and conversion of those products to hydrocarbon fuels produces a fuel within a reasonable estimated cost range. All of the carbon in the biomass is used, including the lignin, which contributes to the favorable cost estimates. Further cost savings might be realized as further process improvement, integration, and optimization occur.

Further work is needed to advance the technologies demonstrated in this project. Conversion of BDO to 2-butanol has been demonstrated, but optimization of the processing conditions and water content of the feed is needed. Catalyst lifetime with aqueous feeds needs to be determined. Optimal catalyst activation methods are required to maximize intermediate and product yields. Integration of the 2-butanol forming process with the fuel forming step or the dehydration step to butenes would provide routes from BDO to a range of fuels and chemical products. Further testing and development of catalysts for conversion of BDO to 1,3-butadiene are needed. Some of this work could be conducted on a 30 cc (of catalyst) scale. Mass and carbon balances would be better defined and sufficient quantities of fuels and products could be produced for property testing.

5 Definitions

1,3BD	1,3-Butadiene
BDO	2,3-Butanediol
CO_2-e	CO_2-equivalents
GC/MS	Gas Chromatography/Mass Spectroscopy
GHG	Greenhouse Gas
GWP	Global-warming potential
IBA	Isobutyraldehyde
IPCC	International Panel on Climate Change
LCA	Life Cycle Analysis
MACRS	Modified Accelerated Cost Recovery System
MEK	Methyl Ethyl Ketone
MVC	Methyl Vinyl Carbinol
OBP	Office of Biomass Programs
TEA	Techno-economic Analysis
WHSV	Weight Hourly Space Velocity

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