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Abstract

Reaction35 is developing a new industrial process that is substantially different from the traditional standalone dehydrogenation process practiced in industry such as Oleflex® and Catofin®. Those processes have substantial energy consumption and loss of feed constraints. The Reaction35 process is based on using molecular bromine to activate the alkane (e.g., n-butane) by forming highly reactive butyl bromides. The butyl bromides are easily converted to n-butylenes (final product) and hydrogen bromide. The hydrogen bromide generated in bromination and dehydrobromination is oxidized with air, recovering the molecular bromine which is reused. The overall result is a process with a favorably low energy consumption and less than 1 % overall loss of feed compared to more than 5 % for the direct dehydrogenation processes.

During the grant period, several important aspects of the technology have been developed further. The major effort was the hydrogenation catalyst step development. The hydrogenation catalyst is used for recovery of the polybromobutanes to the bromobutanes intermediates. The scientific field regarding dibromo- and polybromoalkanes has not been extensively studied, which necessitated that Reaction35 performs a full study of a number of catalysts and the various experimental conditions that influence the hydrogenation reaction. Currently, Reaction35 has completed its catalyst selection and preliminary experimental parameters optimization. This will allow for the construction of an engineering model for a pilot unit testing.

Other processes that were optimized during the grant period were bromination and dehydrobromination under pressure and the rate of reaction of hydrogen bromide and butene in condensed phase. Dehydrobromination experiments showed no cracking products and very small amounts of coke, which is a major point of advantage over the current state of the art standalone alkane to olefins technologies. The results will be useful in creating engineering model for a pilot

design. Reaction35 intends to commence the design and construction of a pilot facility where a closed loop system will be tested on larger magnitude scale and will engage closed recycle loops.

The Grant research also generated a demonstration facility design and a process risk assessment. Those will be used as foundation of the engineering design of the pilot plant.

Overall, the work done using the Grant support is of very high value to Reaction35, and significant advancement in the process development in multiple steps has been achieved. Several of the least understood processes have been studied at industrially-representative conditions. Satisfactory optimization was achieved to next move the testing to a larger, pilot unit.

Acknowledgements.

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List of Figures and Tables.

The list should include the figure/table number, title, and page number. The list of figures precedes the list of tables.

Introduction

Summarized below are project activities for the entire period of funding. These include Tasks 1, 2, 3, 6, 7, 8 that were identified in the Reaction35 Grant application for further research and development to advance the Reaction35 technology. Each task is described, with Reaction35's original hypotheses, the approaches used, and the findings reached in the course of the grant period.

Task 1. Liquid phase selective partial hydrogenation

The Reaction35 technology is based on the ability of bromine to react with alkanes (for example, n-butane) yielding higher reactivity monobromoalkanes (1- or 2-bromobutane). Those monobromoalkanes can be easily converted to the corresponding olefins by either thermal or catalytic reaction. Alkyl bromides have a strong propensity to eliminate hydrogen bromide, forming the desired olefins without forming significant amount of coke or other byproducts and meeting polymer grade specifications without the need for further purification.

One of the most economically desirable results of the Reaction35 technology is the ability to convert substantially all feed(n-butane) into desired product(n-butenes). When bromination takes place, some of the feed acquired more than one bromine atom per molecule making dibromo- and tribromobutanes, which upon catalytic or thermal treatment would not convert to the desired n-butenes and may become material loss in the process. Reaction35's approach to reduce the feed loss is to use a partial selective hydrogenation of the dibromo- and tribromobutanes to monobromobutanes (**eq. 1-2**). These monobromobutanes may be recycled to the bulk monobromobutanes generated in the direct bromination eliminating the potential source for carbon efficiency loss.

$$C_4H_5Br_3 + H_2 \rightarrow C_4H_6Br_2 + HBr \quad (\mathbf{1})$$

$$C_4H_6Br_2 + H_2 \rightarrow C_4H_7Br + HBr \quad (\mathbf{2})$$

$$C_4H_7Br + H_2 \rightarrow C_4H_8 + HBr \quad (\mathbf{3})$$

Hydrogenation of polybromoalkanes is not a heavily-researched field. Reaction35 thus had to discover and perform a variety of performance and stability tests to find a catalyst that may fulfill this purpose. Since selectivity to intermediate state of hydrogenation was sought rather than complete hydrogenation, the targeted catalyst activity was low to moderate. This reduced the probability for the reaction pathway to proceed to full hydrogenation making n-butane (**eq. 3**).

1.1. Design and construction of experimental setup

The experimental setup was built as proposed in the original workplan for the Phase II proposal. All materials of construction were sourced to be corrosion resistant toward the hydrogen bromide that was being generated in the hydrogenation process, including provisions for the small amount of water that might be present as water potentiates the corrosivity of the hydrogen bromide. Mostly all metal pieces were made of Hasteloy®, a high nickel content-based superalloy, and all connectors and gaskets were either Teflon® or other hydrogen bromide-resistant elastomers. A photograph of a hydrogenation laboratory setup is shown in **Figure 1**. Because of the importance of finding a catalyst, which required performing multiple variables testing and long term testing, a total of four practically identical hydrogenation setups have been built like the one in **Figure 1**.

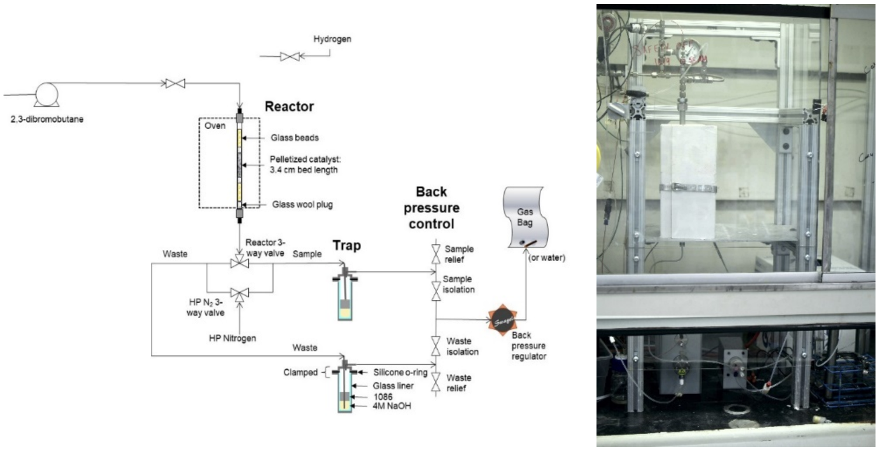


Figure 1. Drawing and a photograph of one of the four hydrogenation setups.

An important improvement that was not proposed in the original proposal was automation of the experiment runs and emergency shutdown procedures allowing for 24 hour operation and running the equipment unattended. The automation was set so that running out of any reagent, loss of pressure or build-up of pressure due to clogging, or electricity instability would shut the experimental system down to preserve the equipment from damage and dangerous leaks. Automation allowed Reaction35 to generate significantly more experimental data and data obtained over higher duration than originally proposed.

1.2. Development of analytical procedures

The hydrogenation of dibromobutanes generates a number of products that are gases or liquids at room temperature. Our analytical goal was to account for at least 95 % of the carbon amount as measured in millimoles (mmol) entering the reactor as feed to be discovered and broken down in carbon mmol equivalent as the various products exiting the reactor, including unconverted dibromobutane feed. The output of the reactor is passed through a liquid trap which captures all liquid products and dissolves some of the gas products as well. The liquid trap is followed up by a gas bag that captures all the gases that have not dissolve in the liquid trap, including the nitrogen that is used to purge the lines used for transporting the products to and from the reactor.

For calibration purposes, all expected and detected products were purchased, standard solutions made, and calibration curves based on at least four concentrations created. The calibration curves along with residence times for the components allowed easy quantification using internal standards that were either present in the liquid trap in known amount or added after sample collection in the gas bag. This was done including not only the various present and anticipated chemical species but also the various isomers that may be generated. Results with carbon balance outside of the 100 +/- 5 % confidence range were not used in drawing experimental conclusions, and tests with concentrations that generated results outside of the confidence range were repeated. The most common source for carbon balances outside of the desired range were either pumps that were drifting outside their delivery calibration range or a leak in the testing system due to the elevated operation pressure.

1.3. Synthesis of Dibromo- and polybromoalkanes

Reaction35 intended to synthesize in our own lab a representative mixture of dibromo- and tribromoalkanes to be used in hydrogenation. Once it was decided that for best results the catalysts have to run 24h a day, the rate of making the dibromo- and polybromobutanes was deemed too high to be sustainable. Instead, Reaction35 was able to source a commercial supplier of 2,3-dibromobutane, which was used instead of internally prepared dibromobutanes. Dibromobutane exists as several isomers, all of which are likely a little different in their reactivity toward hydrogenation. The most common dibromobutane generated in the Reaction35 bromination step is 2,2-dibromobutane, with a smaller amount of 2,3-dibromobutane present. The rest of the potential isomers, e.g. 1,2-, 1,3-, 1,4- and 1,1- are made in less than 0.25 % of the total dibromobutanes content and are not considered valuable for the study.

While 2,2-dibromobutane is the most abundant isomer, we did not subject it to the study for several reasons. According to literature [**1**] and our own internal testing, hydrogenation of geminal dihaloalkanes such as 2,2-dibromobutane is significantly easier compared to any other dibromides due to the halogen of the halogen atoms acting as a destabilizing group for the other one. Importantly, 2,2-dibromobutane is also not commercially available. Thus, 2,2-dibromobutane is not likely to be the rate limiting isomer in the hydrogenation reaction.

In the case of 2,3-dibromobutane, the hydrogenation is more challenging. Nevertheless, achieving selective hydrogenation is just as important with 2,3-dibromobutane. Poor hydrogenation would cause unsustainable build-up of 2,3-dibromobutane in a commercial unit in the step in which the unconverted dibromo-and polybromobutanes feed gets recycled.

1.4. Study of the reaction conditions

The sensitivity of conversion and selectivity of dibromobutanes to monobromobutanes and other products was studied in detail to narrow down the catalyst selection and to identify an optimal range of conditions under which to operate the hydrogenation process. The study can be divided into two subsections. The first one uses catalyst pellets that were ground down and sieved to 150-400 μm particles. Those course particles were used for the operational conditions' optimizations. The second subsection was introduced during the Grant modification, where the ground pellets were substituted with full size pellets to observe their activity, deactivation, and catalytic activity to obtain commercially-meaningful performance and deactivation results. While the results with ground samples are very valuable, they remove external and internal diffusion limitations, wetting inefficiencies, and channeling from being factored in. An actual, commercial reactor has those limitation present at all times because the particles have to be relatively large to avoid unsustainable pressure drop across the reactor bed. To avoid channeling and improve wetting of the full-scale pellets (3 mm extrudates or spheres with 2-4 mm diameter) an inert, fused α-alumina particles in 180-300 μm size range were added as filler to make the results useable while still carry out the experiments in ½ in. diameter tubes. According to rigorous studies reported in the literature, this is a well-accepted approach for obtaining full size catalyst pellets results in small reactor tubes [2,3.

The reaction conditions were tested with the crushed catalyst pellet and the full-size pellets of the same catalyst to allow direct comparison between the results.

1.4.1. *Temperature*

Temperature is likely the most important parameter in chemical reactions. In hydrogenation this is no exception. It is important to determine the range of temperatures in which the selectivity and conversion are optimal. On the low temperature end, the reaction rates are too slow to be practical. If temperatures are too high, side reactions and full hydrogenation will become dominant. Typically, higher temperature speeds up a hydrogenation reaction significantly; however, the selectivity goes down as more chemical reactions become possible.

The study of the influence of temperature on selectivity and conversion was run on crushed catalyst pellets, while keeping the pressure, liquid residence time, catalyst bed length, and the experiment duration identical. The studied temperature range was between 160 and 250 °C. Originally, we had proposed a lower temperature range, but, due to the lower activity by the catalyst we selected, the studied range had to be adjusted higher to achieve a meaningful degree of conversion. The results are presented in **Figure 2**. As expected, we have observed a strong temperature dependence of the conversion corresponding to a reaction with high activation energy. Fortunately, the selectivity toward the desired 2-bromobutane was in excess of 90 % throughout the range except for two highest temperatures. Surprisingly, the loss of selectivity was found to be not due to hydrogenation to n-butane but rather isomerization to other dibromobutanes and hydrogen bromide elimination to bromobutenes.

In conclusion, we have selected 180 °C as an optimal point. The reason for not selecting a higher temperature, even though the selectivity is flat through most of the tested range and conversion is higher at a higher temperature, is to aid the design and safety of operation of the reactor. The hydrogenation reaction is a highly exothermic reaction that also has high activation energy and correspondingly high temperature sensitivity. As a result, an insufficient cooling or a small loss of cooling in an industrial setup may lead to a self-accelerating, run-away reaction with catastrophic consequences. At the same time, a conversion of 20 % per pass corresponds to a reasonably-sized reactor and auxiliary equipment (compressors, pumps, etc.) based on Aspen® engineering suite simulation modeling. Higher per pass conversion improves the economy of the process, but not substantially to merit the increased safety risk, as engineering sensitivity analysis of conversion demonstrated. There also is an appreciable chance that keeping the conversion lower may help with enhancing the lifetime of the catalyst, which is very desirable in commercial applications.

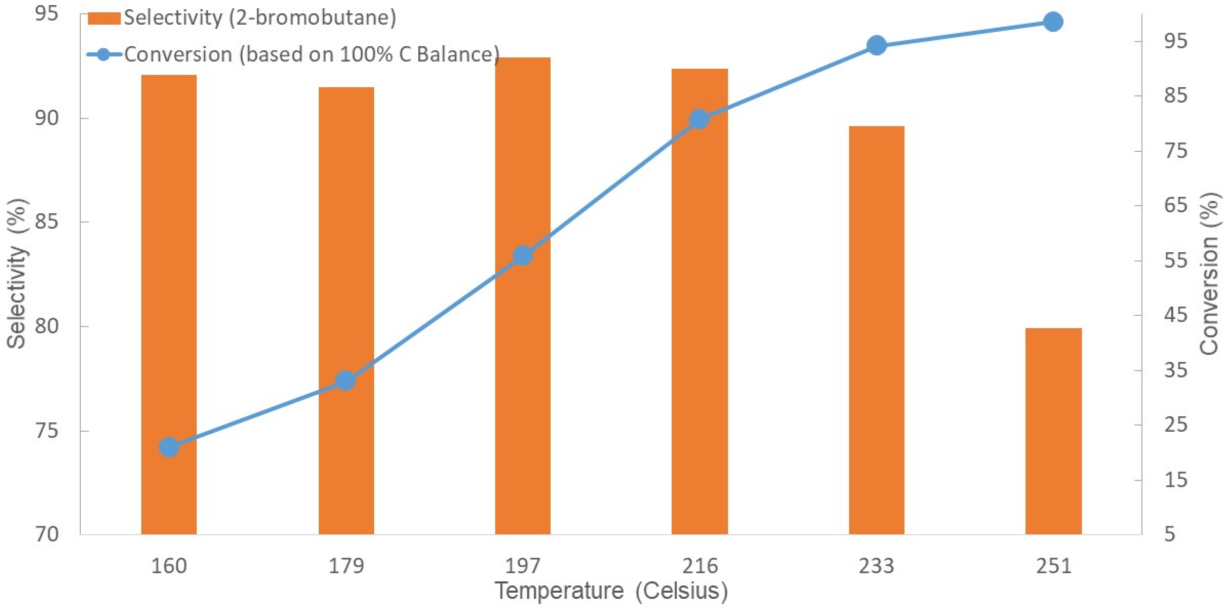


Figure 2. Dependence of the conversion and selectivity of 2,3-dibromobutane as a function of temperature at preselected matching conditions.

1.4.2. Pressure

Pressure is an important parameter in most chemical reactions; however, it is particularly important in hydrogenation reactions. Typically, hydrogen has poor solubility in most liquids and 2,3-dibromobutane is present in a liquid film on the surface of the catalyst particles. Higher pressure accelerates and maintains a higher concentration of hydrogen in the liquid. High pressure also helps with pushing the equilibrium between molecular gaseous hydrogen and adsorbed on the catalyst hydrogen towards the desirable, active form of adsorbed hydrogen which is the real reactive species in hydrogenation. Last but not least, higher hydrogen partial pressure improves the longevity of the catalyst by protecting it from formation of carbides and other surface species that irreversibly destroy surface activity.

Another aspect of pressure is the engineering goal to minimize the volume of reactors and piping by utilizing high pressure wherever possible. Frequently, higher pressure is also beneficial in providing a driving force for reactants flows and may improve separations downstream from a reaction.

In this case the experiments were performed at pressures in the range of 4 to 16 atm (**Figure 3**). The results showed that selectivity improves as the pressure goes higher, while the conversion remains largely flat. An exception for conversion was the lowest pressure point of 4 atm, where the conversion was substantially12 % higher. While there is no easy explanation for the result, the selectivity improvement with higher pressure is more desirable due to reduced need for the impurities management shown in **Figure 4.**

It was concluded that higher pressure is beneficial for the hydrogenation reaction and pressure of 10 atm or higher was recommended for future work and pilot operation.

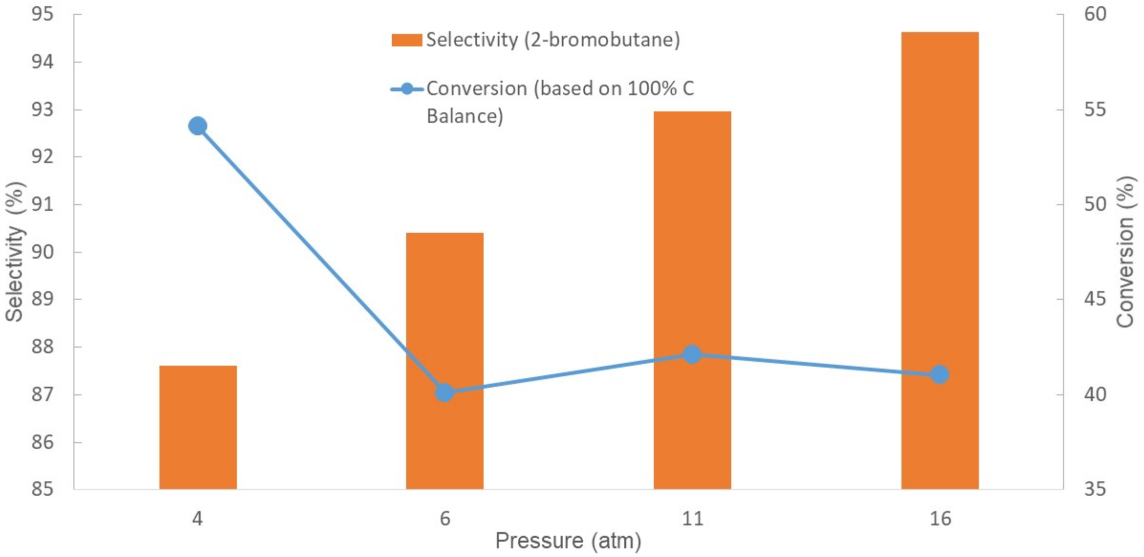


Figure 3. Dependence of the selectivity and conversion of 2,3-dibromobutane as a function of reaction pressure.

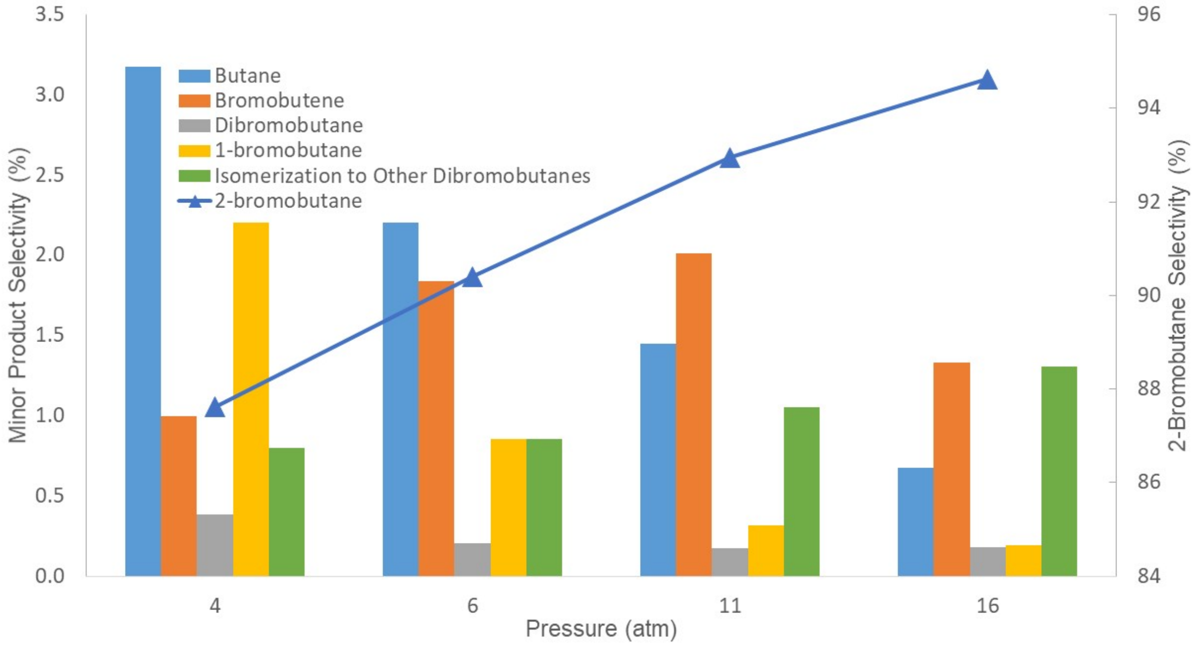


Figure 4. Dependence of the minor product selectivity and 2-bromobutane as a function of pressure.

1.4.3. Excess hydrogen

All hydrogenation reactions in practice are run with appreciable stoichiometric excess of hydrogen. The excess contributes to achieving favorable kinetics in the reaction. However, the critical reason for using excess is to protect the catalyst surface from easy fouling from the formation of surface carbides and polymers from the species that are being hydrogenated. Most catalysts operate with best conversion and selectivity when their surface is heavily covered with adsorbed and dissociated hydrogen. The excess is typically in the range of 2x to 50x. The need for excess is usually balanced by the need for the excess hydrogen to be recycled and reused, which economically favors the lowest ratio that would provide sufficiently good conversion, selectivity, and long lifetime from the catalyst.

In our testing, we fixed the rest of the conditions such as temperature, pressure liquid residence time, and catalyst bed length. The results are shown in **Figure 5**. It appears that for our particular process and catalyst the conversion is largely constant across excess ratios of 4:1 to 16:1. The selectivity favors a lower ratio, which appears reasonable considering that adding more hydrogen accelerates the complete hydrogenation to n-butane, which is the balance of the products (data not shown). The conversion appears steady and the variation in the 87-89 % range is within the margin of experimental error. This result supports the conclusion that 4:1 ratio has best performance. However, the catalyst long-term stability at this ratio has to be confirmed additionally prior to piloting.

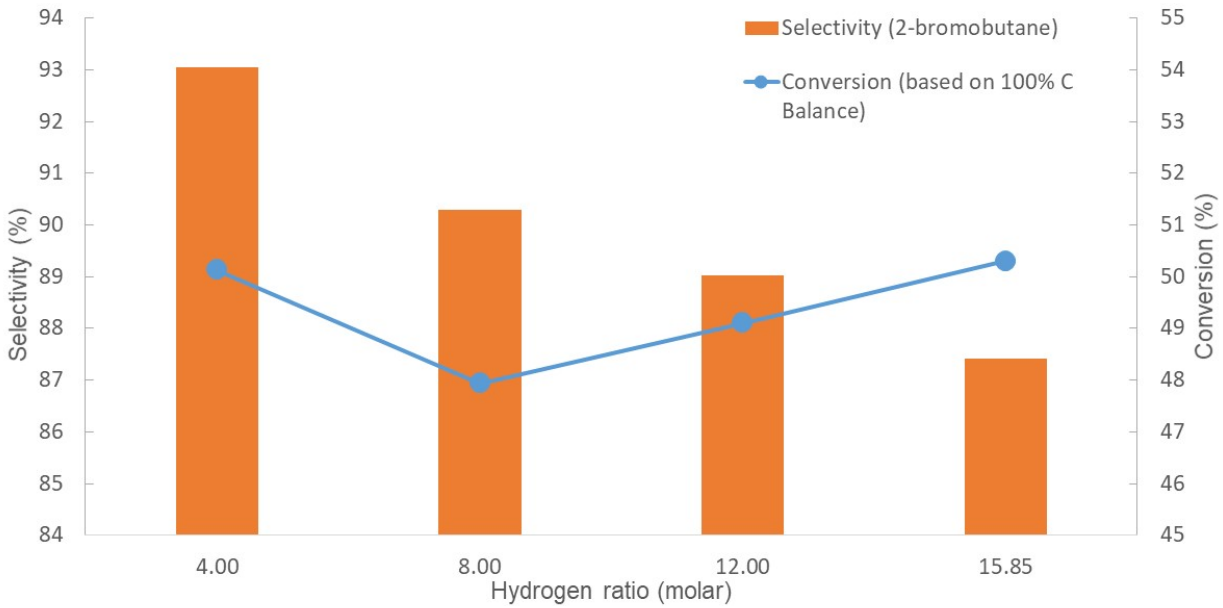


Figure 5. Relationship of selectivity and conversion as a function of the stoichiometric hydrogen excess.

1.4.4. Residence time

In the hydrogenation reaction of 2,3-dibromibutane, the reaction proceeds in a so-called trickle bed regime, where the liquid dibromobutane and the gaseous hydrogen pass through a particulate catalyst bed. In a trickle bed reactor, the flow rate of the liquid is the only factor that is of importance as the gas flow does not change the hydrodynamics of the reactor appreciably until it starts carrying airborne droplets of the liquid reactant [4,5]. Based on our calculation and comparison with similarly-sized reactors, our operation never approached the aerosol mode and was strictly in the trickle bed mode. The liquid flow was determined through calculations based on the dead space of the various hardware fittings and tubes and the holding capacity of the reactor. The nominal gas flow rate was estimated to be in the order of 5-10 s. The results in **Figure 6** show that shorter liquid residence time leads to both lower conversion and selectivity, supporting that the hydrogenation reaction is relatively slow reaction.

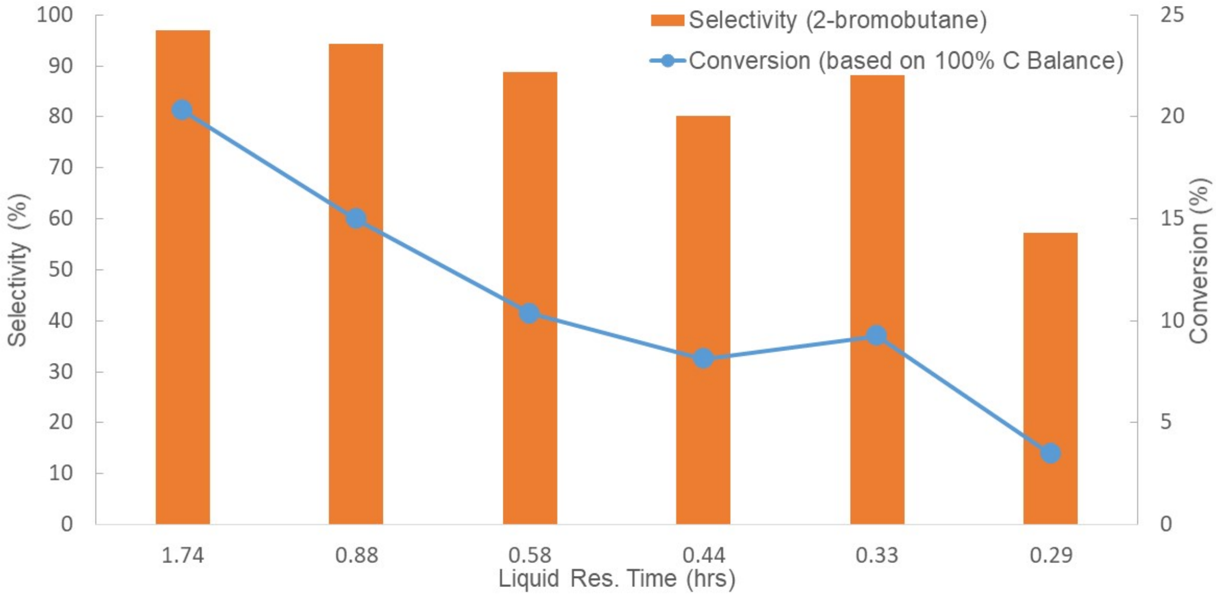


Figure 6. Dependence of selectivity and conversion on liquid residence time. All other experimental parameters such as temperature, catalyst bed length, and temperature were held constant.

1.4.5. Catalyst lifetime

The catalyst lifetime experiment was done using whole pellets instead of crushed pellets. The reason is that the lifetime may strongly depends on the form of the catalyst, and the result on crushed catalyst pellets would not be of value to the further development of the Reaction35 process. To improve the gas and liquid distribution of the feed, the catalyst pellets were embedded in a filler of 180-400 μm fused α-alumina particles. This approach of distribution of large pellets in relatively small reactor is considered a well-accepted method for studying pellets that are otherwise too large for the test reactor diameter. The experiments were run 24 hours a day with an experiment being paused only by a failing component of the setup. Once failed parts were replaced, the experiment was restored back to operational conditions.

Two approaches were used: constant conditions testing and constant conversion testing. In constant conditions testing, the experiment was run at optimized, pre-selected conditions and samples tested daily for performance decrease over time. In a constant conversion experiment, the conversion was the maintained parameter with temperature being increased at 1 ^{o}C increments over time to maintain the initial performance of the catalyst. The results for a constant conversion run are shown in **Figure 7**. The results support that the catalyst tested in a full-size pellet form has the desired performance that can be maintained at the desired 20 % per pass conversion, with small, occasional increases in temperature. The tested catalyst was tested in excess of 4.5 months with the temperature increased only 8 ^{o}C with appreciable room for further increases based on other experiments which showed that a temperature of up to 210 ^{o}C does not have an immediately detrimental effect on the catalyst.

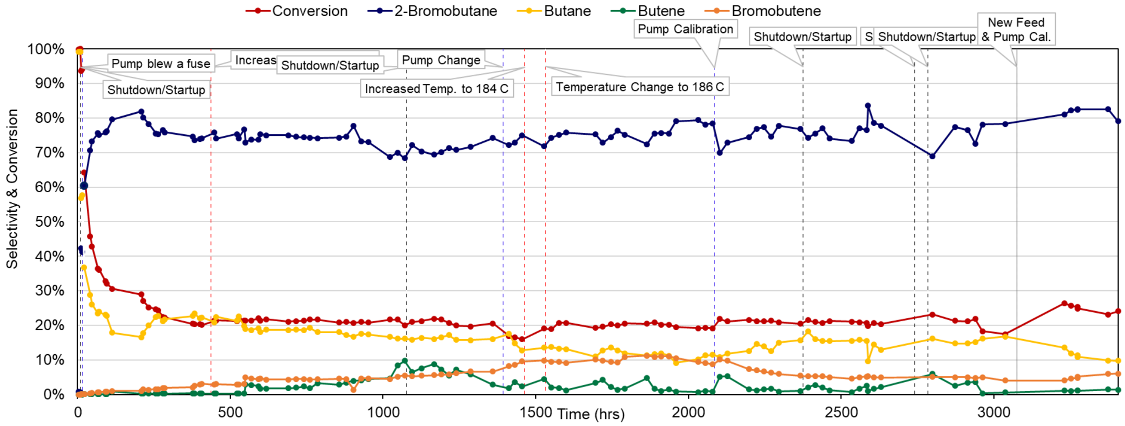


Figure 7. Selectivity and conversion as a function of the time on stream of the selective hydrogenation reaction.

1.4.6. Catalyst characterization

The catalyst was characterized before and after 1500 h on stream used for active component sintering using hydrogen chemisorption. The chemisorption allows the determination of the percentage of active metal on the surface. When sintering takes place, the dispersion decreases appreciably. For a catalyst that has been on stream for ~1500 h, a test showed that the metal dispersion was 84%, which corresponds to excellent dispersion. For a never-used catalyst, a dispersion in the range of 85-95 % is typical. It was concluded that sintering did not take place in the tested catalyst system and was not responsible for the catalyst deactivation.

SEM with EDX (Energy Dispersive X-Ray) elemental analysis has been performed on catalyst pellets selected from different depths of the catalyst bed: close to the top, middle, and close to the bottom of the reactor. The EDX allowed us to observe carbon deposited as coke in cross-section of the pellets, showing that coking increases with the catalyst bed depth. For example, the pellet at the top of the bed had less than 10 at. % carbon, which grew to 14 at. % in the middle and reaching a 33 at. % C high at the pellet from the bottom of the bed. The starting catalyst tested negative for carbon presence. Our hypothesis is that the catalyst deactivation is due to coking of the oligomerization products of some of the butenes generated in the hydrogenation reaction. Those side products grow in concentration along the bed as the conversion to butenes and bromobutenes grows higher.

1.4.7. Different polybromoalkane reactants

Several bromine-containing species were tested as test solutions in 2-bromobutane to determine their behavior in hydrogenation reaction. The reason for that is that a majority of the reactions are sequential so a product may appear generated in the reaction by not appearing in the feed and being present in the end of the reactor. However, in the industrial setting those compounds will be recycled back to the hydrogenation reactor and be present in the feed, such as bromobutenes and tribromobutanes. It was the purpose of the work in the task to verify that those chemical species will be successfully hydrogenated and would not accumulate in the recycle stream.

2-bromo-2-butene is a common impurity that is generated in the bromination and dehydrobromination process. Small amounts are observed generated in hydrogenation, when pure 2,3-dibrombutane is used as a feed. The purpose of the experiment is to demonstrate that the typical hydrogenation catalyst at operational conditions would hydrogenate the 2-bromo-2-butene to separable products and that, if fed in the hydrogenation reactor, would result in a net consumption of bromobutenes (of which 2-bromo-2-butene is the most common isomer present). The results were that in the temperature range of 160 to 210 °C, 11 atm., and 4:1 hydrogen excess, 2-bromo-2-butene was converted to n-butane with 94-98 % selectivity with the balance of 1.5- 2 % converted to butene. The conclusion is that the hydrogenation process would be a net consumer of bromobutenes and when recycled it would exhaust them to extinction.

2,2,3-tribromobutane was tested as a feed diluted with 2-bromobutane at optimal hydrogenation conditions (temperature range of 160 to 210 °C, 11 atm., and 4:1 hydrogen excess). Approximately 99 % of the tribromobutane was consumed yielding dibromobutanes and bromobutanes. The yield to the product of thermal decomposition to dibromobutenes was less than 1 %. As expected, tribromobutane was easier to hydrogenate than dibromobutanes and monobromobutanes and becomes completely consumed in a single pass through the reactor. The conclusion is that the hydrogenation process would be a net consumer of tribromobutanes and when recycled they would be exhausted to extinction.

1.4.8. Determination of internal diffusion limitation

Due to the relatively low rate of the reaction and the need for fairly high residence time (see ***1.4.4***) it was determined that internal diffusion could not be a limiting factor in the catalyst performance. To observe diffusion limitations, the process of diffusion has to be the rate limiting and the diffusion in and out of the pores to be slower than the reaction rate. However, the hydrogenation reaction is relatively slow, making it a rate limiting step in the studied temperature range. The results agree with fact that the hydrogenation catalyst that was used has small pore volume (below 0.05 cm^3/g) and large macropores. Diffusion in large macropores typically is not a diffusion issue, except for very fast reactions.

1.4.9. Determination of the external film diffusion limitation

Due to the relatively low rate of the reaction and the need for fairly high residence time (see ***1.4.4***), we determined that film diffusion is not a limiting factor in the catalyst performance. To observe film diffusion limitations, the film diffusion should be slower than the reaction rate on the catalyst surface. We have observed a strong dependence on liquid flow rate, supporting the conclusion that the reaction is kinetically limited and unlikely to be external film diffusion limited.

1.4.10. Long term testing of commercial pellet size (1.8-2.7 mm dia.) in preselected optimal conditions of operation.

Long term testing is a critical part of the development of commercial catalyst. For the long-term study, the leading catalyst candidate was subjected to several different regeneration procedures. Those procedures are targeting to extend the life of the catalyst in the reactor as long as possible, preferably for at least one year. Reaction35's goal was to establish and maintain a minimum conversion per pass to achieve economically-reasonable reactor size.

The regenerations were performed using diluted air targeting gradual oxidation of carbonaceous deposits, while minimizing any structural changes to either the support or the dispersed catalyst metal. This was achieved by mixing nitrogen and oxygen in a ratio that provides 2-5 vol % of oxygen. The temperature of regeneration was started at 250 ^{o}C and gradually increased to 350 ^{o}C as the regeneration progressed. The regeneration was considered complete once the carbon dioxide generated in the regeneration became a trivial amount (as measured by TCD detector) using a gas bag to capture the gases leaving regeneration. The results of two different regenerations are shown in **Figure 8**. The selectivity and conversions were also closely watched when unexpected shutdowns took place to determine the effect of loss of feed and/or temperature and pressure.

It was observed that regenerations highly increase the n-butane production along with overall increase in conversion, which corresponds to restoration of the most active sites of the catalyst.

Following regeneration, the conversion exceeded the preset target of 20 % per pass conversion with acceptable selectivity. Thus, it was determined that the lifetime of the catalyst may be extended to one year or longer by occasional regeneration as needed to restore the desired conversion above the desired minimum conversion of 20 % per pass.

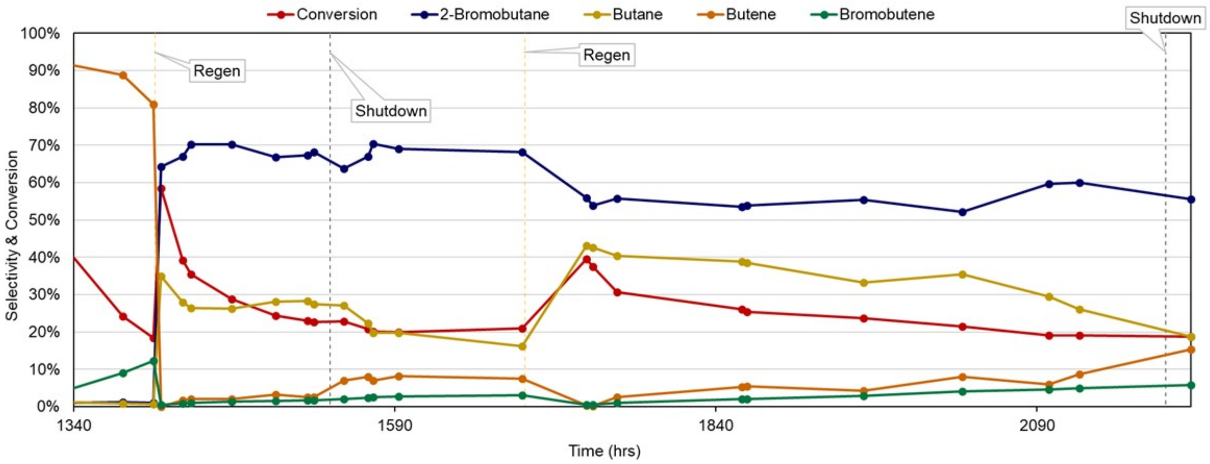


Figure 8. Dependence of selectivity and conversion as a function of time on stream. Regenerations and shutdowns are labeled on the time segment shown in the graph.

Task 2. Study of the liquid phase hydrobromination

2.1. Design and construction of experimental setup

In the Reaction35's process, n-butyl bromides are dehydrobrominated to form hydrogen bromide and the final product mixture of n-butenes. The effluent of the dehydrobromination reactor contains a mixture of unconverted 1-bromo and 2-bromobutanes, n-butenes, and hydrogen bromide. The purpose of the liquid phase hydrobromination task is to determine the rate of the reverse reaction of the hydrogen bromide and butenes in condensed phase back to the starting feed of bromobutanes. An extensive reverse reaction will require a significant recycling and recirculation of the unconverted bromobutanes. If that stream is large enough, it may endanger the economics of the entire process. Residence time and temperature appear to be the two main "levers" that may be changed to achieve separation that is economically favorable.

The hydrobromination setup was designed to provide a realistic viewpoint for the rate of reaction in the separation column where all the dehydrobromination products come together in a liquid phase. Hydrogen bromide, 2-butene, and 2-bromobutane were fed using calibrated, metering pumps into a heated mixer where the components were allowed to evaporate, dwell for a preset time, and then move to condense in a condenser and react with each other for a known amount of time under pressure sufficient for the components to condense. The temperature of the condenser was controlled actively with a chiller thermostat.

The schematic of the experimental setup is shown in **Figure 9.**

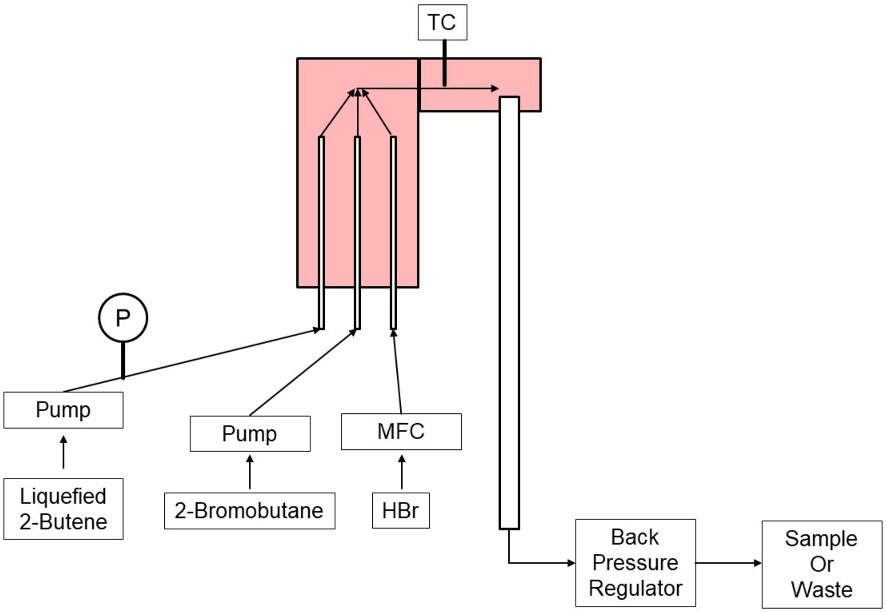


Figure 9. Scheme of the setup used for studying hydrobromination of 2-butene in condensed phase.

The setup was designed from materials that can handle the elevated pressures and the corrosivity of all the input and output stream such as fluorinated elastomers and highly corrosion-resistant nickel-based alloys. The temperature in the condenser, where the reverse reaction takes place, was controlled by a thermostat with circulating fluid that maintained constant temperature. Once the sample spent a pre-set time in the condenser allowing accurate determination of the residence time, the reactor flow passed through a back-pressure regulator and collected in a sample trap which would contain sodium hydroxide. This stopped the reaction and allowed measurement by GC of the amount of generated bromobutane.

2.2. Development of analytical procedure

Analytical procedures were designed to determine the extent of the chemical reaction taking place in the experimental setup. The goal was to achieve as close as possible to 100 % carbon balance, meaning that all the carbon content in the organic species entering the reactor are accounted for in the final organic products. The species that were quantified are 1- and 2-bromobutanes and the corresponding 1-butene and 2-butene. While the GC calibration was capable of detecting and measuring trace amounts of any byproducts such as n-butane, isobutene, and butadienes, none were ever detected in the conducted experiments.

2.3 Study of the reaction conditions

2.3.1. Temperature

The effect of temperature of the condensed liquid phase on the rate of the reversed reaction of hydrogen bromide and butene was not well known and was studied under this Grant. While the equilibrium is not favorable upon cooling down and even in gas conditions, the rate of the reverse reaction in gas phase is slow (halftime of more than 5 minutes).

To emphasize the differences in conversion as a function of temperature, two temperatures were tested: 10 ^oC and 60 ^oC. The results for a given residence time showed a strong temperature dependence that became smaller as the residence time became lower. At high residence time, the reverse reaction was only 13 % at 10 ^oC and 52 % at 60 ^oC; for the shorter residence time, the difference was from 40 to 86 % at the two temperatures.

We are cautious to draw any conclusions as the results were difficult to reproduce and the repeated experiments gave a widespread range in results (average results reported). However, the overall trend is that lower temperatures of operation correspond to lower conversions of the butene product back to bromobutanes.

2.3.2. Residence time

The residence time study was important to evaluate how much time the condensed butenes and hydrogen bromide may spend together in condensed phase before they react back to the starting mixture of bromobutanes. While the equilibrium is very favorable at high temperatures where the dehydrobromination takes place, the reverse reaction was found to be appreciably fast in condensed liquid phase [6]. If the reaction is found to be faster than the typical 30-120 s that a component spends in a distillation column with average number of trays, a non-distillation separation would be necessary prior to condensing the mixture that would either remove preferentially hydrogen bromide or butenes.

When the coolant was set to maintain 10 °C for the condensed phase experiment, and the butenes and hydrogen bromide were fed in stoichiometric ratio for a long residence time (~1000 s), the reverse reaction to bromobutanes consumed as much as 79 % of the fed butenes. When the residence time was set for an intermediate duration of 720 s, the reverse reaction progressed, consuming 40 % of the butene. For a short time period of 500 s, the reverse reaction consumed only 13 %.

These results suggest that economically acceptable separation of the hydrogen bromide and the butenes, corresponding to at least 20 % per pass conversion, is achievable. While the hydrobromination reaction is relatively fast, a quick separation and low residence time distillation column may afford fast enough separation for economic feasibility.

Task 3. n-Butane bromination at pressure

Bromination of n-butane is the first step of the Reaction35 process. It includes the homogenous phase, non-catalyzed direct reaction of molecular bromine with n-butane. While the reaction has been performed at various experimental conditions, pressure was never studied due to the significant technical difficulties with delivery and evaporation of liquid bromine. At room temperature, bromine is highly corrosive. While atmospheric pressure experiments can be performed using glass and fluorinated plastics equipment, those cannot be used at elevated pressure.

Elevated pressure is an important parameter to study in bromination because of the product distribution of the minor products. These are formed in equilibrium, such as bromobutenes and dibromobutanes and tribromobutanes (**equation 4 and 5**). Alternatively, even though the reactions of bromination of n-butane to bromobutanes are not expected to be heavily influenced by pressure due to no volume change in the reaction, its change in kinetics may still be noticeable because of non-ideality of the reacting compounds.

$$C_4H_6Br_2 \rightleftharpoons C_4H_5Br + HBr \quad (\mathbf{4})$$

$$C_4H_5Br_3 \rightleftharpoons C_4H_4Br_2 + HBr \quad (\mathbf{5})$$

The reason is that the dibromobutanes and bromobutenes follow different paths if separations occur after the bromination reaction. It is possible that due to the Le Chatelier principle, the amount of bromobutenes will be significantly lower while the dibromobutanes will be correspondingly higher. The dibromobutanes are heavy boiling compounds that separate easily and are routed to the hydrogenation reactor. Bromobutenes, on the other hand, are similar to bromobutanes in volatility, causing them to transport together and load different nods of the separation's infrastructure.

3.1. Design and construction of experimental setup

The setup was designed to use glass syringe pumps to deliver the liquid bromine to avoid corrosion of metal pumps and their components. Corrosion products are capable of catalyzing side reactions in the bromination reaction such as hydrogen bromide eliminations that may skew the obtained results.

The bromine and butane were evaporated by passing them independently through Hasteloy® coils loaded with quartz sand inside a heated oven at temperature exceeding the boiling temperature at the elevated operation pressure. The bromine and n-butane vapors were mixed in a mixing T-shaped tube prior to passing them through the reactor embedded in a heating block (**Figure K**). This setup ensured that the bromination of n-butane reaction is performed in conditions as close as applicable to the industrial setting envisioned for the Reaction35 process.

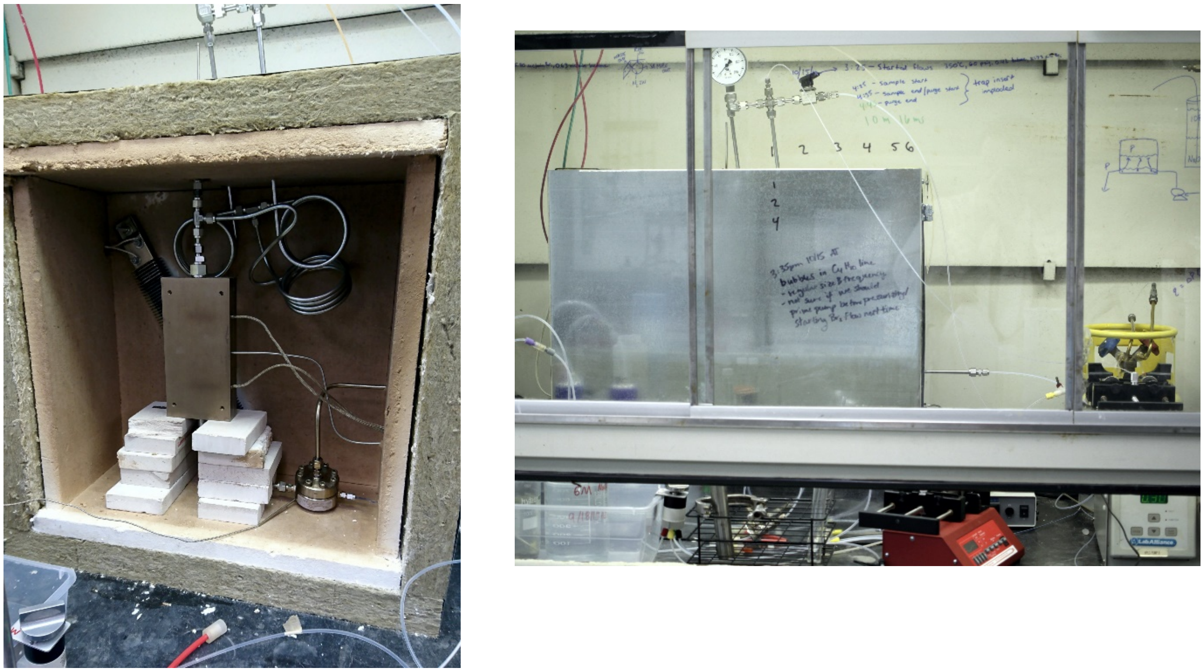


Figure 10. Photographs of the n-butane bromination setup.

3.2. Development of analytical procedures.

GC quantitative methods have been developed for all major and minor products that occur or may occur in the bromination reaction. Those include all isomers of butenes, butanes, bromobutanes, and dibromobutanes. Since the products and feed of the bromination reaction are liquids and gasses, the various materials were calibrated on two separate GC instruments equipped for injection of liquid or gas samples correspondingly. The quantification was handled by using quantitative calibration curves using internal standard which was either present in the capture trap (for liquids) or added once the sample was collected for gases. All samples were quantified for their carbon mmol content to verify that all the feed is accounted for in the product stream.

3.3. Study of the reaction conditions

3.3.1 Temperature

Bromination was performed as originally proposed at 375 °C, however a significant soot formation was observed in the product trap. Soot formation is typically a sign of excessively high temperature and as a result the study was performed at the lower 325 and 350 °C. The results showed that while 2-bromiobutane was the major product, a significant amount of butenes were observed (**Figure 11A**) along with appreciable amount of 1,3-butadiene. This finding support a hypothesis that while bromination works as expected, the fact that the high pressure experiment was conducted in metal tube instead of he quartz tube used in the atmospheric pressure experiments has made a catalytic contributions towards the products by causing dehydrobromination of the bromobutanes (to butenes) and bromobutenes (to 1,3-butadiene). It is also likely that the high pressure accelerated the reaction to high extent, causing most of the residence time in the reactor to be by the final products, enabling the formation of additional byproducts in amount significantly higher than expected. It appears that further studies will be necessary to find the optimal temperature for the butane bromination process.

3.3.2. Residence time

Residence time is one of the really important parameters in the bromination reaction. During the radical propagation reaction of bromination, the duration at given conditions will determine if all the elemental bromine will be consumed or not. Unconverted bromine is particularly undesirable downstream of the bromination reactor due to its really high corrosivity. Using excess butane along with sufficient residence time consumes all molecular bromine to undetectable levels. Along with the molecular bromine being converted, the mixture of bromination products participates in a number of side reactions such as dehydrobromination, disproportionation and isomerization. This hypothesis is supported by the observed results (**Figure 11B**).

At reference duration of 12 s (100 % RT) the butane conversion reached 21 % with 2-bromobutane and butenes as major products with small amounts of 1,3-butadiene, dibromobutane and bromobutenes. When the residence time was reduced to 80% RT (9.5 s) the conversion was down to about 15 % with apparently significant part of the bromine being used in the formation of dibromobutanes (26 %). It appears that the additional few seconds residence time led the dibromobutanes to comproportionate with the present unconverted n-butane leading to higher yield of 2-bromobutane and butene and dibromobutanes amount going down from 26 to 3 % (**Figure 11B**).

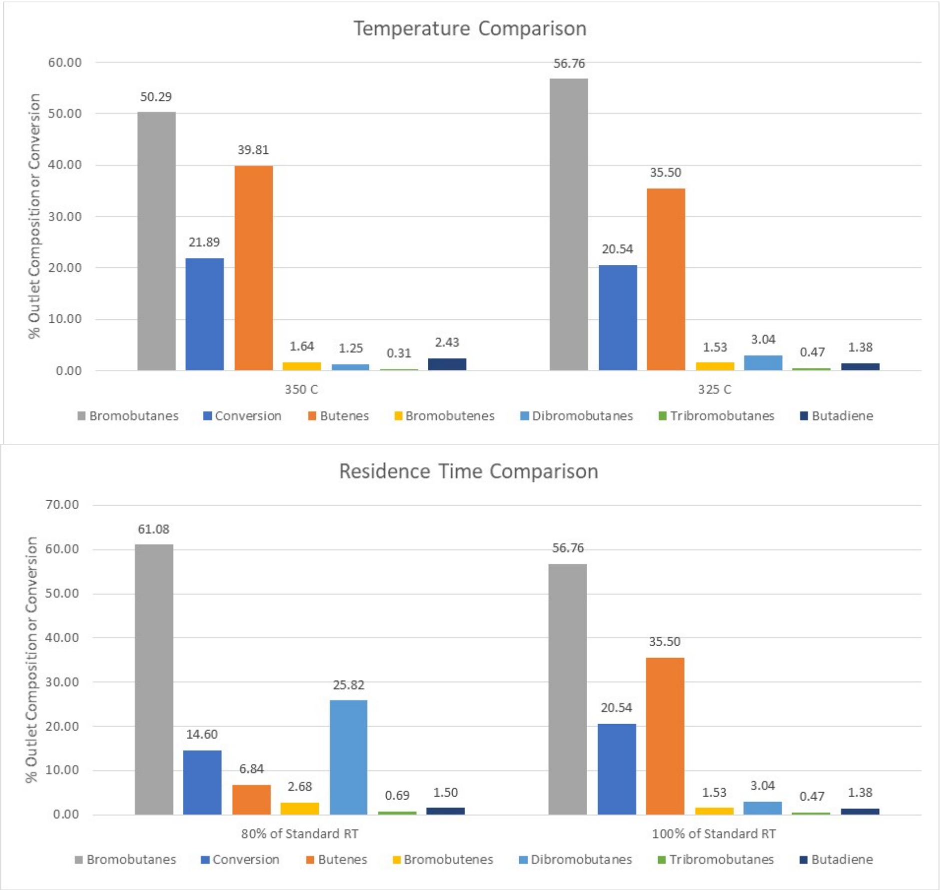


Figure 11. Dependence of the conversion of n-butane bromination as a function of **A)** temperature and **B)** residence time. Bromine to butane ratio is 0.5, 100 % standard residence time is 12 s.

Task 6. Process risk assessment

In Objective Six, information obtained in completion of Objectives 1 through 5 of the Phase Two Work Plan was evaluated monthly in a process risk assessment to identify its impact on the knowledge gaps and risks that i) remain in the technology and ii) must be eliminated or mitigated in the Demonstration Facility to enable the technology to advance to the commercial scale at a high level of confidence for successful operation. The results of the process risk assessments were incorporated into the Conceptual Engineering Models and pro forma economic models. Thus, these results helped Reaction35 to evaluate and quantify the advantages projected for the Reaction35 Technology, thereby ensuring that the magnitude of the advantages remain under the increased accuracy of the revised models. Reviews were conducted in collaboration with consulting industry experts. These experts were asked to conduct the assessment from the perspective of a consultant who has been retained by an investor who is contemplating the purchase of a license from Reaction35 for subsequent construction of a commercial facility. They key deliverable was completed and can be seen in **Table 1**.

Description of Risk	Mitigation to Manage Risk
Dehydrobromination	
Poor single pass conversion of 1 and/or 2-bromobutane. Greater accumulation of bromobutane in the recycle loop reducing the plant capacity.	**Operation**: Final reactor design must have extra built-in capacity
Oversizing the reactor for risk mitigation. 1) Unnecessary residence time and 2) increased coke formation.	**Operation**: 1) Ensure reactor is able to vary the amount of catalyst to vary residence time and that external heaters have flexibility to adjust with packing changes 2) Build flexibility into the demo that allows it to run at lower temperatures/conversions to suppress coke formation
Coking rate is higher than anticipated.	**Operation**: Build flexibility into the demo that allows it to run at lower temperatures/conversions to suppress coke formation
Selectivity to C4 byproducts is higher than acceptable.	**Operation**: Build flexibility into the demo that allows it to run at lower temperatures/conversions to suppress side reactions
Steady state di/tri-bromobutane or di/mono-bromobutenes reactor feed concentration is greater than expected. Increased coke and product impurity yields.	**Operation**: Build flexibility into the demo that allows it to run at lower temperatures/conversions to suppress coke formation
Decomposing coke catalyzes side reactions to undesirable products. Increased product impurity yields.	**Operation**: Build flexibility into the demo that allows it to run at lower temperatures/conversions to suppress side reactions
Unable to quantify between isobutylene and 1-butene in liquid GC samples in Santa Barbara. Isobutylene liquid yields considered 0; therefore, 1-butene yields may be lower and isobutylene higher.	**FEL-2**: Conduct sensitivity analysis to determine worst-case impact
Kinetic data has not been collected. Unable to rigorously design reactor heat transfer and temperature profiles.	**FEL-3**: Collect kinetics
Corrosion products cause plugs downstream.	**Operation**: Using high-temperature corrosion-resistant materials **Operation**: Coupons in reactor **Operation**: Sacrificial filter in between reactor stages
Excessive ambient heat loss from quasi-isothermal reactors not properly accounted for in plant design. Inability to reach necessary temperature for high conversion.	**Operation**: Design of shell-side heating system with oversized heating duty for start-up and operation.

Hydrogenation	
Unknown impurity is made that cannot be removed in current distillation scheme	**FEL-3**: Create list of components that may show up but have not been observed on the GC. Once this list has been created, we can map where they would end up in the current distillation scheme and implement a purge stream on the distillation column
Representative feed not used which may affect catalyst and overall reactor performance compared to simulation/HMB.	**FEL-3**: Experiment co-feeding HBr (or N_2 if solubility is comparable) **FEL-3**: Experiment co-feeding 2BR-BA & HBr
Testing completed with 2,3-dibromobutane, while most common isomer is expected to be 2,2-dibromobutane. Conversion/selectivity of demo facility could therefore be skewed if 2,3-dibromobutane is not representative of all other isomers	**FEL-3:** Test multiple isomers
Realistic feed composition may significantly change the hydrodynamics and phase of the reactor (e.g. changing from trickle bed to vapor-phase) which may affect catalyst and overall reactor performance compared to simulation/HMB.	**Operation**: Design reactor under assumption of vapor-phase (including extra equipment needed for trickle bed). **Operation**: Recirculate liquid effluent to force liquid phase **Operation**: Raise total pressure (& design reactor for higher pressure)
Unknown mass transfer coefficients leading to undersizing reactor.	**Operation**: Oversize reactor
Unknown liquid holds up leading to hot spots in reactor which could lead to adverse effects on selectivity and uncertainty in predicting pressure drop.	**Operation**: Liquid pump-around. Design reactor to accommodate for better distribution.
Unknown catalyst wetting efficiency leading to undersized reactor.	**FEL-3**: Upflow operation of lab reactors (or alternate lab reactor design) **Operation**: Over-size reactor
The hydrobromination of butenes/bromobutenes may not be as reactive as what is being assumed	**FEL-3**: Test Hydrobromination
There is the possibility that the catalyst is capable of regeneration, but that it cannot maintain conversion/selectivity for long enough to allow for an economic regeneration cycle (if catalyst stability is not adequate without regeneration).	**Operation**: Catalyst can be regenerated off-line or swapped for fresh catalyst.

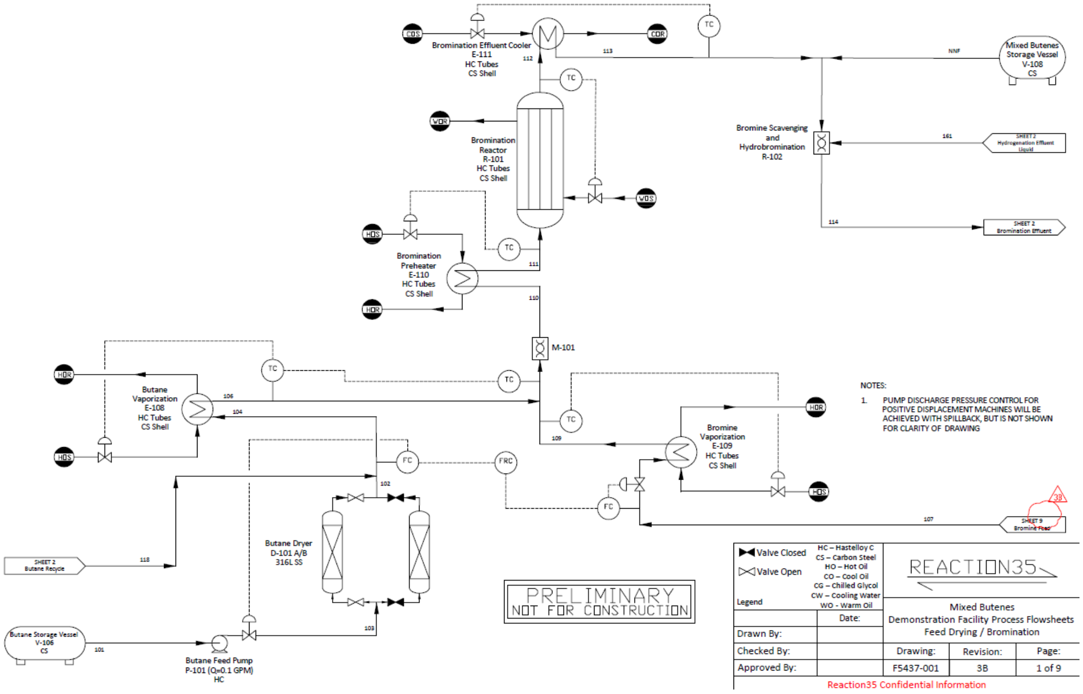
Catalyst deactivation may not follow a trend and suffer significant deactivation beyond ~5 months which would require the catalyst to be replaced or regenerated before anticipated.	**Operation**: Dual Hydrogenation reactor system
Pd based catalyst slowly reacts with bromine making $PdBr_2$	**Operation**: Increase Pd loading **Operation**: Increase catalyst bed depth **FEL-2**: Investigate oxidation state of catalyst after long-term run(s)
Catalyst poisons are unknown	**FEL-3**: Research what poisons would be likely for a Pd catalyst
Selectivity, but not conversion, degrades as temperature increases	**Operation**: Optimization of temperature ramp **Operation**: Selectivity measured as a function of temperature on used catalyst
Not having a predictive kinetic model leading to (1) difficulty in setting and tuning control parameters to achieve steady state operation and/or mitigate upsets, (2) difficulty predicting how upsets affect other sections of the process, and (3) undersizing/oversizing reactor.	**Operation**: Over-designed liquid re-circulation **Operation**: Surge capacity for accumulation of effluent
Simulation pressure does not match experimental data due to simulation trying to match hydrogen partial pressure which may affect overall reactor performance compared to simulation/HMB.	**FEL-2/3**: Experiment co-feeding HBr (or N_2 if solubility is comparable) **Operation**: Varying overall pressure to mitigate change in performance based on different partial pressure in lab vs Demo **Operation**: Fix overall pressure and reducing partial pressure fo H_2
VLE based on PSRK may not properly define the system.	**Operation**: Oversize affected equipment
Bulk of reaction occurs in a narrow zone in the reactor, causing heat removal issue	**Operation**: More inert material to spread out reaction zone
Reaction exotherm is greater than expected.	**Operation**: Lower feed temperature (if feasible) **Operation**: Circulate liquid. **FEL-3:** Perform calorimetry test **FEL-3:** Review heat of formation data / Aspen data source

Catalyst leads to water formation in the reactor causing corrosion.	**Operation**: Assure complete removal of water sources from catalyst. **FEL-3:** Investigate temperature & time needed to dry catalyst
Hydrogen solubility in liquid product exceeds design.	**Operation**: Oversize H_2 stripper and other affected equipment
Hydrogen excess required exceeds design.	**Operation**: Oversize affected equipment.
Hydrobromination	
Reverse reaction destroys product, greatly increasing the necessary size of the reactor and associated separation equipment	**Operation**: Add the partial condensation unit operation to minimize product loss
Reverse reaction has a greater than anticipated effect on net single pass conversion, even with partial condensation implemented	**Operation**: Final reactor design must have extra built-in capacity
di-/tri-bromobutanes may not be able to get out of the second separation train	**Operation**: Route bromobutane recycle loop through the distillation column responsible for monobromobutane separation from di-/tri-bromobutanes
Bromination	
Lack of kinetic data	**Operation**: The Demonstration Facility bromination reactor will be sized assuming a linear temperature profile. The reactor will include an over specification of tubes to account for heat management difficulties. The shell side heat transfer system will be designed to accommodate higher and lower setpoints to adjust with the reaction rate.

Table 1. Process risks analysis and their corresponding potential solutions and workarounds.

Task 7. Demonstration facility design

In this objective, the Design Team reviewed the following in a series of meetings and/or web conferences: i) the engineering models of the conceptual commercial-scale olefin facilities and ii) the mitigation / elimination plan for each knowledge gap or risk. A preliminary design basis that addresses each knowledge gap or risk and the information required for mitigation was established for the Demonstration Facility. Through this analysis, the scale of the Demonstration Facility that would enable the collected information to be used directly to design commercial scale facilities was determined as 6 kg/h of olefin product. The key deliverable from Objective 7 was completed and is shown in Figures x-y. This deliverable consists of a complete set of Process Flow Diagrams from which the Demonstration Facility may proceed directly to the FEED stage.



NOTES:

1. PUMP DISCHARGE PRESSURE CONTROL FOR POSITIVE DISPLACEMENT MACHINES WILL BE ACHIEVED WITH SPILLBACK, BUT IS NOT SHOWN FOR CLARITY OF DRAWING

Mixed Butenes
Demonstration Facility Process Flowsheets
Feed Drying / Bromination

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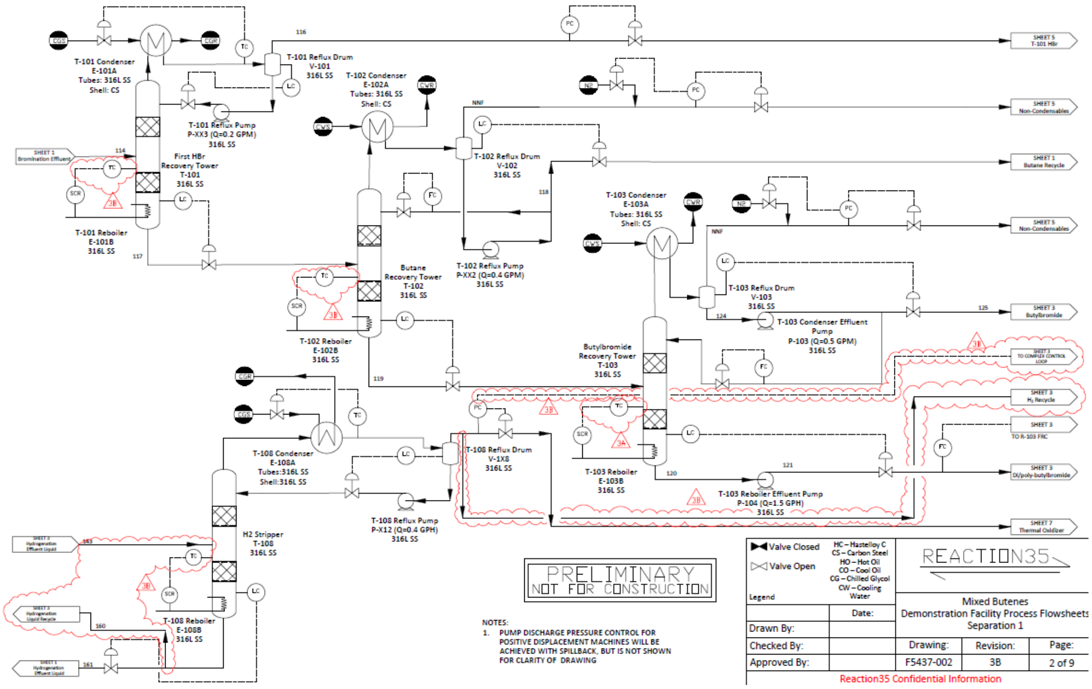
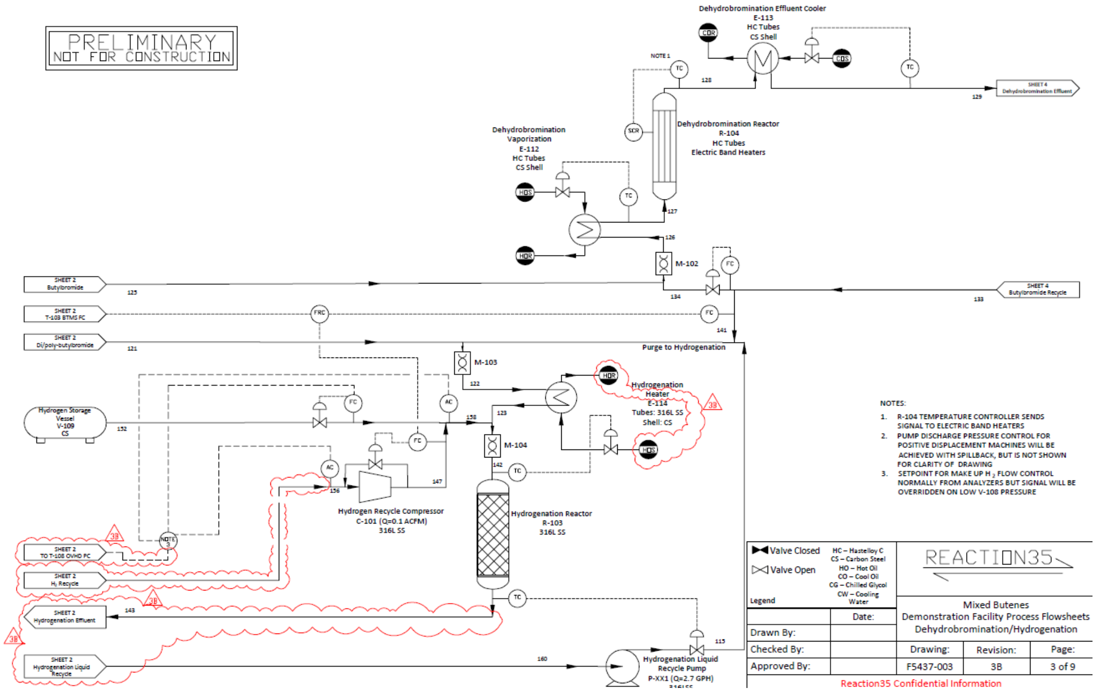
Checked By:		Drawing:	Revision:	Page:
Approved By:		F5437-001	3B	1 of 9

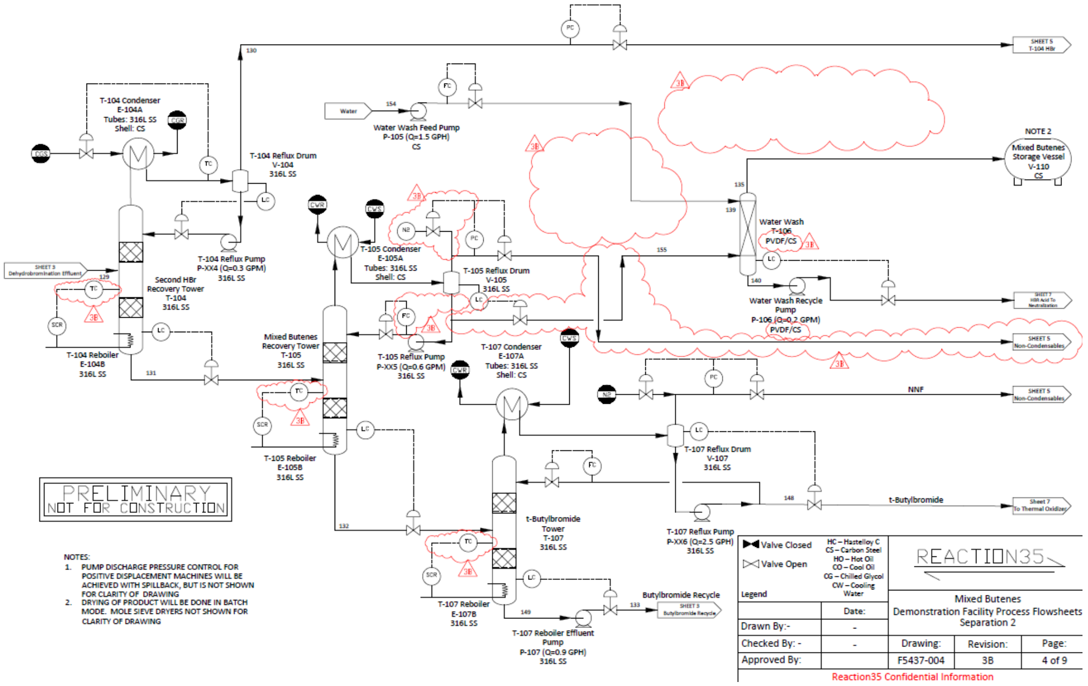
Reaction35 Confidential Information



NOTES:
1. PUMP DISCHARGE PRESSURE CONTROL FOR POSITIVE DISPLACEMENT MACHINES WILL BE ACHIEVED WITH SPILLBACK, BUT IS NOT SHOWN FOR CLARITY OF DRAWING



NOTES:
1. R-104 TEMPERATURE CONTROLLER SENDS SIGNAL TO ELECTRIC BAND HEATERS
2. PUMP DISCHARGE PRESSURE CONTROL FOR POSITIVE DISPLACEMENT MACHINES WILL BE ACHIEVED WITH SPILLBACK, BUT IS NOT SHOWN FOR CLARITY OF DRAWING
3. SETPOINT FOR MAKE UP H_2 FLOW CONTROL NORMALLY FROM ANALYZERS BUT SIGNAL WILL BE OVERRIDDEN ON LOW V-108 PRESSURE



NOTES:

1. PUMP DISCHARGE PRESSURE CONTROL FOR POSITIVE DISPLACEMENT MACHINES WILL BE ACHIEVED WITH SPILLBACK, BUT IS NOT SHOWN FOR CLARITY OF DRAWING
2. DRYING OF PRODUCT WILL BE DONE IN BATCH MODE. MOLE SIEVE DRYERS NOT SHOWN FOR CLARITY OF DRAWING

◀▶ Valve Closed ▷◁ Valve Open Legend	HC – Hastelloy C CS – Carbon Steel HO – Hot Oil CO – Cool Oil CG – Chilled Glycol CW – Cooling Water	REACTION35		
	Date:	Mixed Butenes Demonstration Facility Process Flowsheets Separation 2		
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Approved By:		F5437-004	3B	4 of 9

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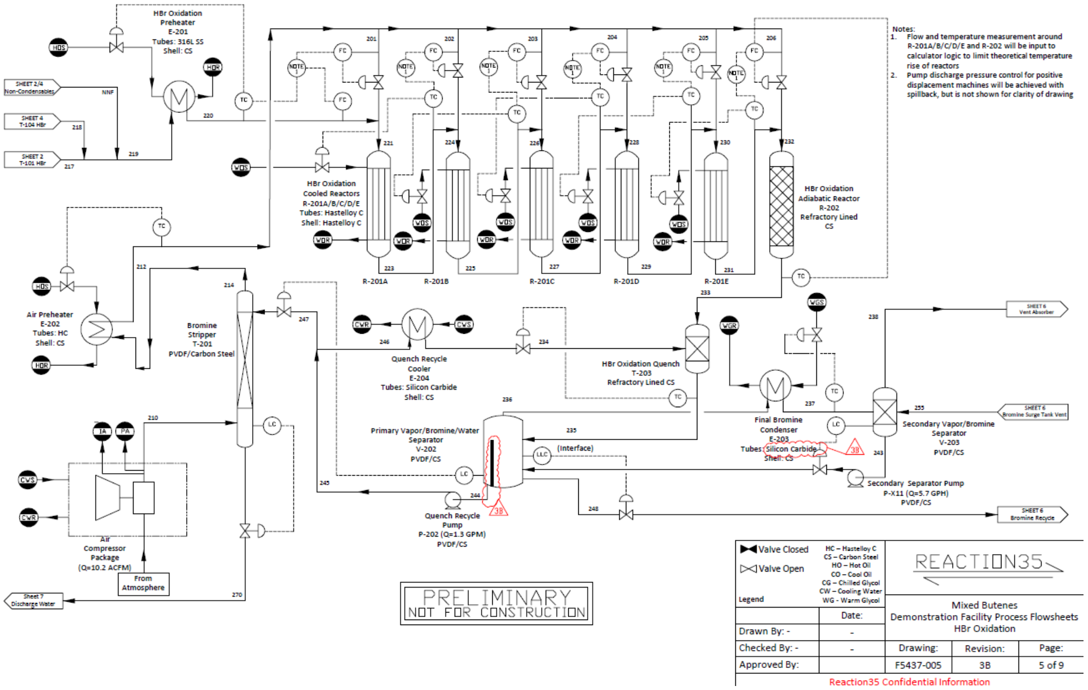

Notes:

1. Flow and temperature measurement around R-201A/B/C/D/E and R-202 will be input to calculator logic to limit theoretical temperature rise of reactors
2. Pump discharge pressure control for positive displacement machines will be achieved with spillback, but is not shown for clarity of drawing

◀▶ Valve Closed ▷◁ Valve Open Legend	HC – Hastelloy C CS – Carbon Steel HO – Hot Oil CO – Cool Oil CG – Chilled Glycol CW – Cooling Water WG - Warm Glycol	REACTION35		
	Date:	Mixed Butenes Demonstration Facility Process Flowsheets HBr Oxidation		
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Approved By:		F5437-005	3B	5 of 9

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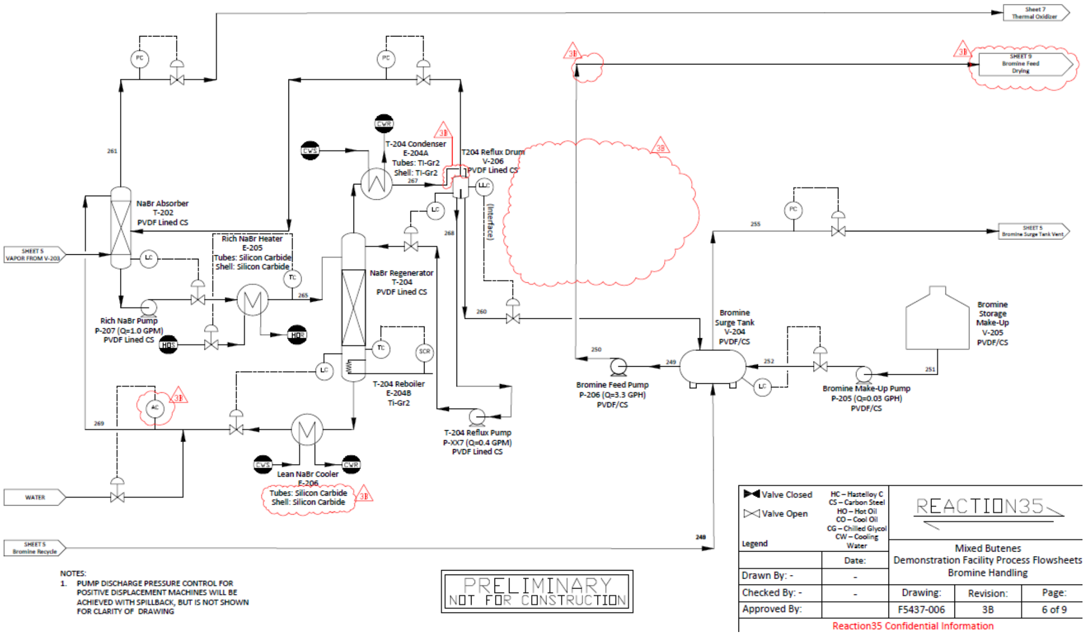

NOTES:
1. PUMP DISCHARGE PRESSURE CONTROL FOR POSITIVE DISPLACEMENT MACHINES WILL BE ACHIEVED WITH SPILLBACK, BUT IS NOT SHOWN FOR CLARITY OF DRAWING

Mixed Butenes
Demonstration Facility Process Flowsheets
Bromine Handling

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Approved By:		F5437-006	3B	6 of 9

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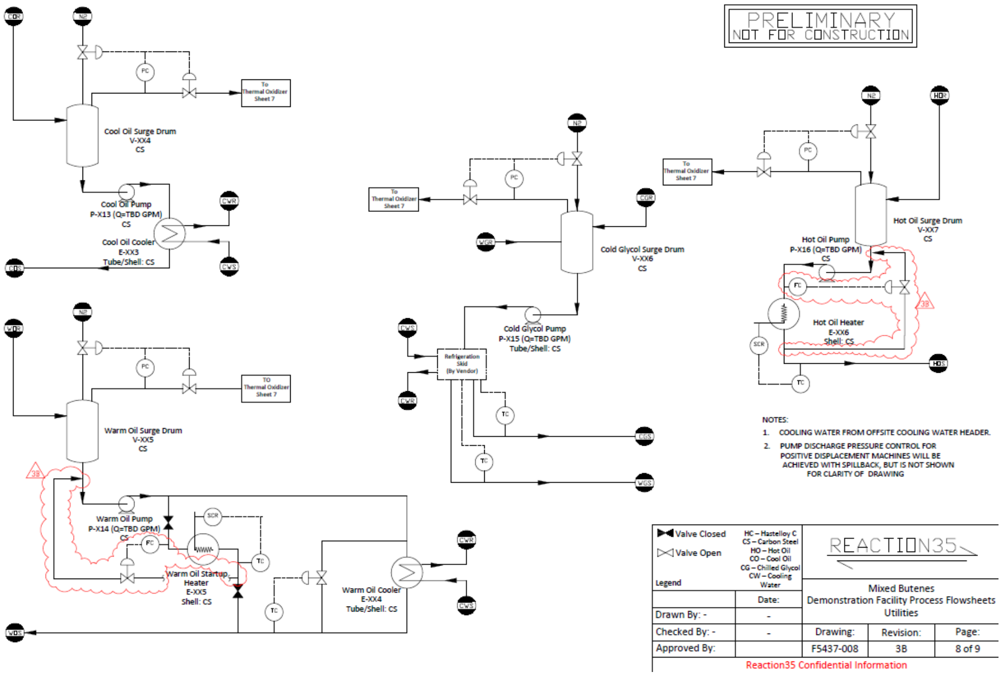

NOTES:
1. COOLING WATER FROM OFFSITE COOLING WATER HEADER.
2. PUMP DISCHARGE PRESSURE CONTROL FOR POSITIVE DISPLACEMENT MACHINES WILL BE ACHIEVED WITH SPILLBACK, BUT IS NOT SHOWN FOR CLARITY OF DRAWING

Mixed Butenes
Demonstration Facility Process Flowsheets
Utilities

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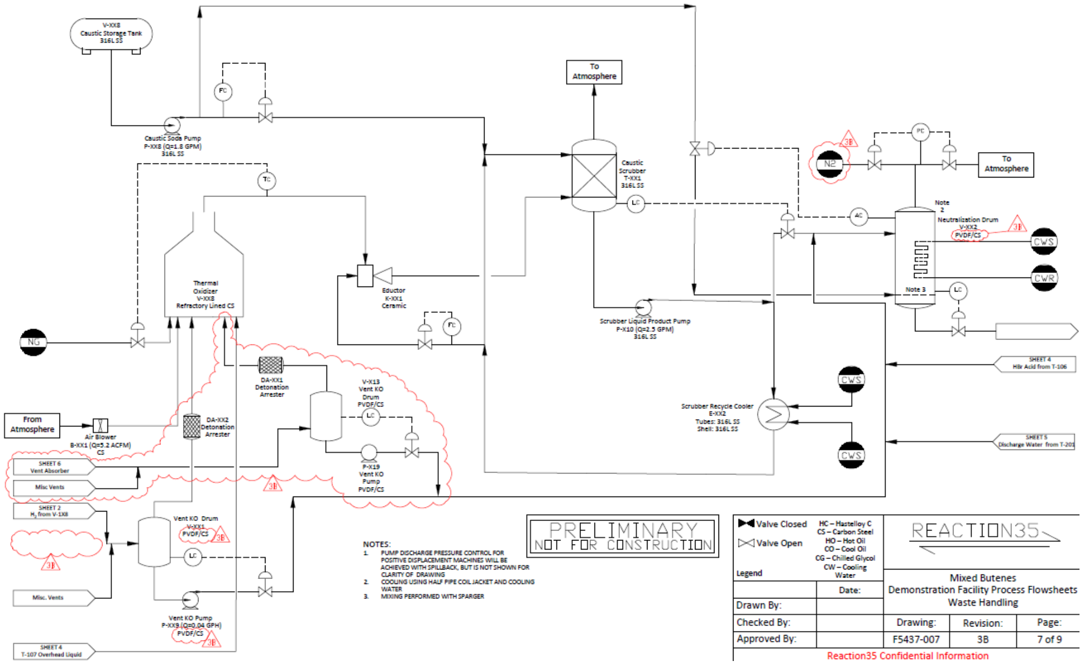

NOTES:
1. PUMP DISCHARGE PRESSURE CONTROL FOR POSITIVE DISPLACEMENT MACHINES WILL BE ACHIEVED WITH SPILLBACK, BUT IS NOT SHOWN FOR CLARITY OF DRAWING
2. COOLING USING HALF PIPE COIL JACKET AND COOLING WATER
3. MIXING PERFORMED WITH SPARGER

PRELIMINARY
NOT FOR CONSTRUCTION

▶◀ Valve Closed
▷◁ Valve Open
Legend

HC – Hastelloy C
CS – Carbon Steel
HO – Hot Oil
CO – Cool Oil
CG – Chilled Glycol
CW – Cooling Water

REACTION35

Mixed Butenes
Demonstration Facility Process Flowsheets
Waste Handling

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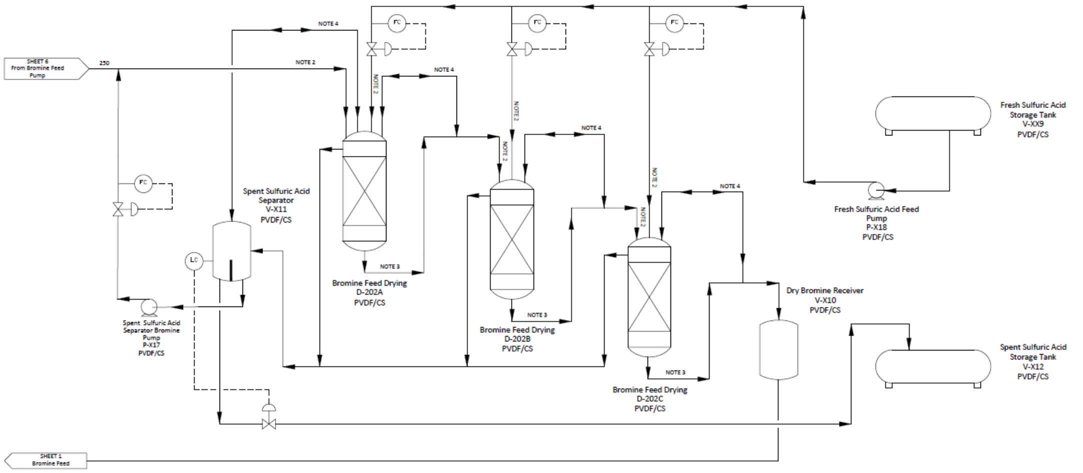
Approved By:		F5437-007	3B	7 of 9

Reaction35 Confidential Information



NOTES:
1. PUMP DISCHARGE PRESSURE CONTROL FOR POSITIVE DISPLACEMENT MACHINES WILL BE ACHIEVED WITH SPILLBACK, BUT IS NOT SHOWN FOR CLARITY OF DRAWING
2. ENTERS VESSEL THROUGH DIP LEG. DIP LEG NOT SHOWN
3. SEAL LEG . HOLDS BROMINE LEVEL IN UPSTREAM VESSEL
4. PRESSURE EQUALIZATION LINE.

PRELIMINARY
NOT FOR CONSTRUCTION

▶◀ Valve Closed
▷◁ Valve Open
Legend

HC – Hastelloy C
CS – Carbon Steel
HO – Hot Oil
CO – Cool Oil
CG – Chilled Glycol
CW – Cooling Water

REACTION35

Mixed Butenes
Demonstration Facility Process Flowsheets
Bromine Drying

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Reaction35 Confidential Information

Task 8. Dehydrobromination of bromobutanes at elevated pressures

Dehydrobromination is a key step in Reaction35's technology which converts the butyl bromide to a mixture of n-butenes and eliminates hydrogen bromide. The reaction could be done either catalytically or thermally. The goal is to achieve a product quality of the butenes that can be classified as 'polymer grade' and can be used for making polybutylene and other mixed elastomers. Polymer grade is the highest grade of commercially marketed butylene.

8.1. Design and construction of experimental setup The experimental setup was designed to deliver precisely metered amounts of 2-bromobutane or 1-bromobutane to a pressurized reactor using an HPLC pump (**Figure 12**).The exit of the reactor was purged with nitrogen to reduce residence time of the products in condensed phase and eliminate the reverse reaction in condensed phase. The products were passed to a waste container and switched to sampling for a preset, measured amount of time. The equipment was designed from highly corrosive materials to withstand the corrosion of hydrogen bromide that is generated in the reaction.

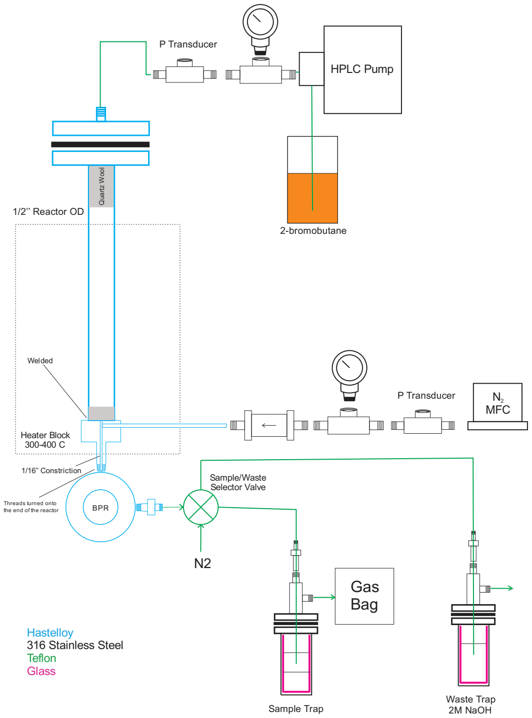

Figure 12. A scheme of the experimental setup used for dehydrobromination studies of 2-bromobutane/1-bromobutane.

8.2. Development of analytical procedures

The products of dehydrobromination of bromobutanes generates 1-butene and 2-butene as major products. All expected products and byproducts that are present in the specifications of the polymer grade butylene were calibrated for by determination of their retention time in GC. Since some products are captured in a liquid trap and others in a gas bag, the calibration was performed on two different GCs, one equipped for injection of liquid and another for gas samples. The quantification of the species was done using internal standard that was made present in the capture trap for the liquids and added to the gas bag to the collected gas samples. A typical target was achieving 100 +/- 5 % C mmol balance between feed and all measured products.

To observe and quantify the carbon dioxide and carbon monoxide generated in oxidation regeneration (decoking) another GC with a TCD detector was equipped with a ShinCarbon ST packed column capable of separation of the air components. The carbon monoxide and carbon dioxide were measured on the TCD detector using quantitative calibrations curves for the species.

8.3 Study of the reaction conditions

The dehydrobromination reaction was studied by varying temperature, residence time, and the presence of catalyst. The results obtained in absence of catalyst are summarized in **Table 2** and interpreted in the sections below.

Pressure (psig)	Temperature (°C)	Flowrate (g/min)	Conversion (%)	Feed
0	150	0.04	98.9	2-bromobutane
14.7	375	0.44	16.4	2-bromobutane
14.7	425	0.41	70.2	2-bromobutane
14.7	425	0.44	64.5	2-bromobutane
75	425	2.2	37.2	2-bromobutane
162	425	4.4	9.3	1-bromobutane
14.7	425	0.44	8.1	1-bromobutane
165	425	1.07	29.8	1-bromobutane

Table 2. Table of results obtained in absence of catalyst (thermal dehydrobromination).

In presence of catalyst, the reaction of dehydrobromination was run at various temperatures and residence times to evaluate the sensitivity of the reaction rate to temperature (related to activation energy) and the performance of the catalyst. There is no benefit in making a commercial catalyst bed longer than necessary to establish equilibrium between the species.

8.3.1. Temperature

As shown in **Table 2**, the conversion for no catalyst present case is strongly dependent on the temperature. For example, operation at 375 °C vs. 425 °C sees the conversion to butenes change from about 16 to 70 %. It is known from literature that 1-bromobutane decomposes more slowly than 2-bromobutane, and our results concur with that finding. At identical pressure, temperature, and residence time (425 °C, 14.7 psig and same flow rate) the 1-bromobutane conversion is merely 8. 1% vs. 70.2 % for 2-bromobutane. This result is important because 1-bromobutane is likely to accumulate in the recycle loop due to its appreciably lower conversion rate, even though its presence in the bromination feed is fairly low at below 5 %.

When a catalyst was used, the conversions at a fixed residence time as a function of temperature was obtained (**Figure 13**). The catalyst accelerated the dehydrobromination of both 1-bromo- and 2-bromobutane which was a desirable result.

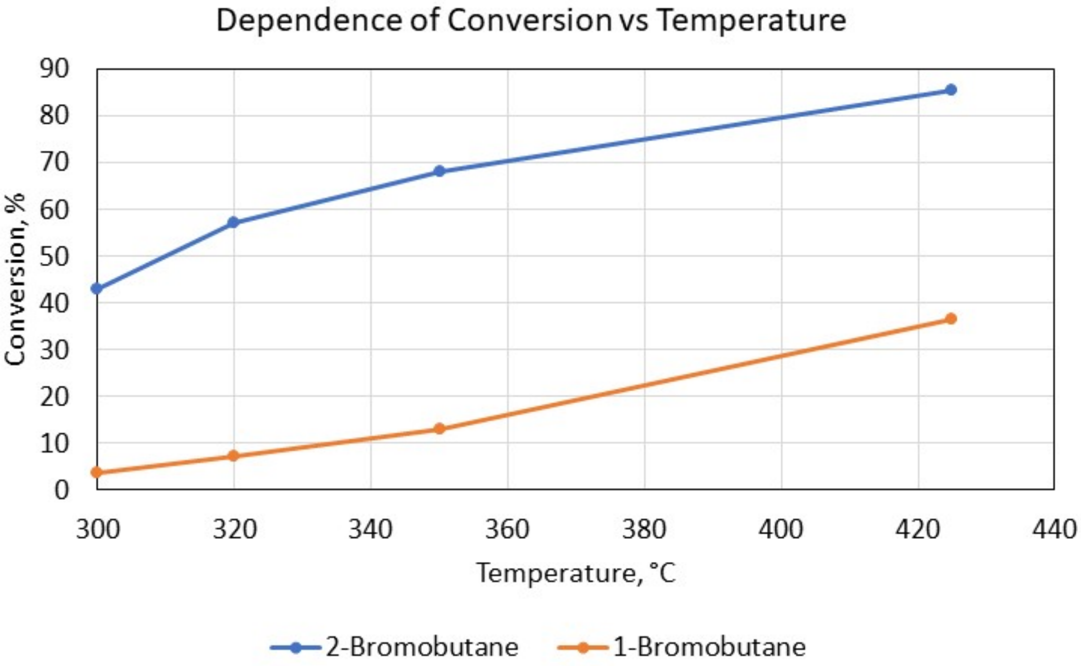

Figure 13. Dependence of conversion of 1-bromobutane and 2-bromobutane as a function of temperature with a 5 cm catalyst bed and 5 s residence time at 1 atm pressure.

8.3.2. Residence time

Residence time is important reaction parameter as it should be closely linked to the performance of the dehydrobromination process. It should closely match the data as the reaction approaches equilibrium to design optimal reactor size for high conversion.

In the case of 2-bromobutane a fivefold higher flowrate (2.2 vs 0.44 g/min.) leads to halving of the conversion (**Table 2**). For 1-bromobutane at identical conditions, a decrease in residence time four-fold reduced the per pass conversion down to a third (29.8 vs 9.3 % conversion).

For the case when catalyst was used, the time to reach equilibrium was sought. The reaction was run at constant 275 ^{o}C, and the residence time was varied to accomplish this purpose. The results (**Figure 14**) show that for 2-bromobutane the equilibrium likely is in the 100 s range at about 45 % equilibrium conversion. For 1-bromobutane the conversion kept going up with time, and equilibrium was not reached within the residence times tested in experimental design exceeding 180 s.

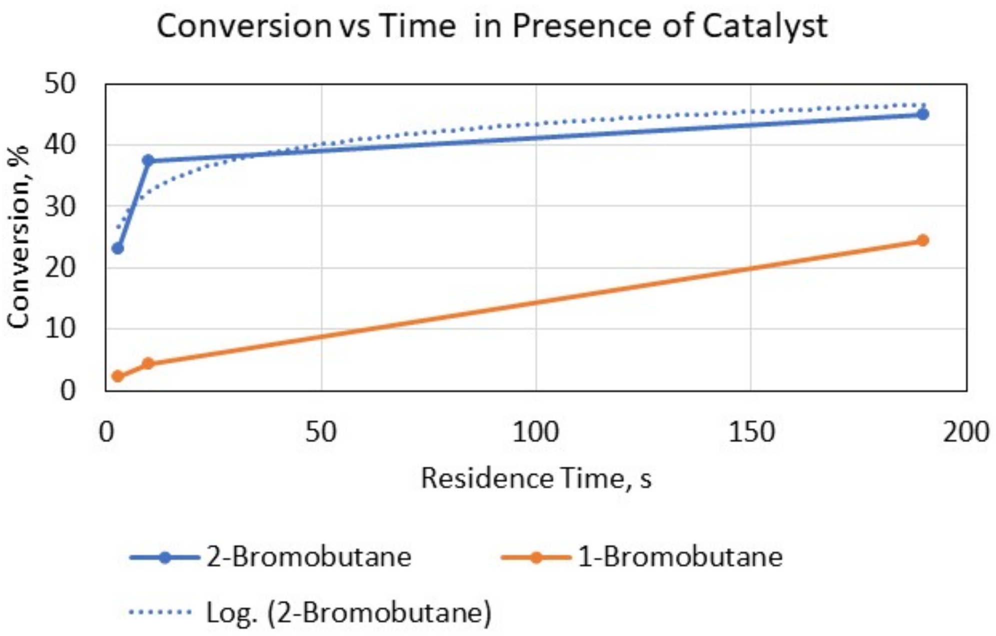

Figure 14. A graph of the conversion as a function of time in presence of catalyst. t=275 °C, pressure 1 atm.

8.3.3. Catalysts

Several different catalysts were sourced and tested. A commercially available pelletized catalyst was selected as a leading candidate. The benefit of using catalyst is the faster reaction and smaller reactor. However, the drawback (in addition to higher cost) is that typically the higher surface area of a catalyst is responsible for appreciably more coking, which takes time to be removed by oxidation and must eventually be replaced from time to time. As shown in **Figures 13** and **14,** a catalyst significantly improves the kinetics of the reactions.

The comparison of thermal versus catalytic dehydrobromination allowed Reaction35 to select a catalyst, perform thorough kinetic testing, and evaluate how multiple regenerations influence the catalyst performance over multiple cycles.

8.4. Determine conditions of oxidative catalyst regeneration

The catalyst has a maximum operation temperature at 475 °C which limits the rate at which coke may be removed by oxidation. Coke oxidation is highly exothermic reaction, which required the use of diluted air to reduce the oxidation rate and the local heat generated over the catalyst. We started a regenerating stream containing 5 % O_2 at 400 °C and increased the temperature to 425 °C once the evolution of CO_2 and CO subsided, which led to a smaller amount of coke left on the catalyst.

8.5. Coke accumulation rates measurements.

The coke was measured by passing air or oxygen through either empty tube (thermal dehydrobromination) or one with catalysts used for a known amount of time. The temperature was raised to 400 °C, and the amount of CO_2 and CO was determined. The coking rate was calculated as a percentage of the coke carbon amount in mmol divided by the carbon amount in mmol of feed passed through the reactor/catalyst system. In the experiments without the use of catalyst, the coking rate was mere 0.0023 %. This result supports the expectation that a thermal dehydrobromination reaction will accumulate coke at a very low rate and thus that the coke will need to be removed very infrequently, probably annually.

In the case of catalyst, when coke was measured by measurement of the CO_2 and CO using a GC equipped with TCD detector, it was determined that the coke amount was 0.249 %. While substantially higher than the non-catalyzed reaction, the coke rate is small enough that the catalyst will likely be functional for more than a week prior to deactivation, the catalyst will need to be regenerated. Most importantly, no cracking products such as C1, C2, and C3 were ever observed even in trace amounts in the dehydrobromination. This is a very important determination as it confirms the advantage the Reaction35 technology has over the current standalone dehydrogenation technologies such as Catofin® and Oleflex®. In those established technologies, at least 5 % of the feed per pass becomes destroyed by becoming coke or cracking products. The separation of the cracking products requires elaborate separation columns, and the excessive coke formation requires very frequent decoking.

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