Molten Salt Chemical Looping for Reactive Separation of HBr in a Halogen-Based Natural Gas Conversion Process

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Abstract

Hydrogen bromide (HBr) oxidation to molecular bromine (Br₂) is demonstrated in a chemical looping process using a molten bromide salt. The two-step process is operated at 500 °C and first contacts oxygen with molten KBr-LiBr-NiBr₂ to form Br₂ gas and a suspension of nickel oxide (NiO) particles in one reactor. The oxide suspension is then contacted with HBr to regenerate the bromide salt and produce steam. Sixty-eight metal oxides/bromides were considered. The cyclic interconversion between oxide and bromide, by alternating exposure to HBr and oxygen, at a single temperature was only possible with nickel. In contrast to solid-based chemical looping systems, the liquid bromide salt (NiBr₂ dissolved in KBr-LiBr eutectic) was found to be cycleable without attrition or deactivation. Further, when mixtures of olefins and hydrogen bromide were reacted with the oxide suspension, selective oxidation of HBr was observed without hydrocarbon oxidation. High selectivity for HBr oxidation is due to the solubility of HBr in the molten salt, which allows contact with NiO, whereas, the insoluble hydrocarbons do not contact the reactive oxide. A process model that makes use of reactive separation of HBr from hydrocarbons and process intensification using molten salt-based chemical looping is presented as a potentially lower cost alternative to a process model using conventional separations in bromine-based methane conversion. The total heat exchanged in a corrosive environment in the molten salt based process is 205 MW, and the heat exchanged in a corrosive environment in the conventional process is 581 MW.

Keywords

Process intensification, halogenation, methane, molten salt, HBr, gas-to-liquids, bromine

1. Introduction

Natural gas will be available globally as a relatively low-cost feedstock for many decades. Economical use of methane in natural gas as a feedstock for liquid chemicals and fuels continues to be a long-term scientific and engineering challenge [1-3]. Demonstrated processes have high capital costs and require large scales to be profitable. Commercially competitive gas-to-liquid (GTL) processes have relied on the formation of synthesis gas and its subsequent conversion to methanol or linear alkanes using Fischer-Tropsch chemistry [4]. Carbon dioxide emissions from these processes are significant; large capital costs and risks of future costs associated with carbon dioxide emissions have limited GTL process deployment using synthesis gas-based processes.

An alternative pathway for methane partial oxidation using bromine, rather than oxygen, has been demonstrated and piloted [5-9]. Bromine can be generated from the reaction of oxygen with hydrogen bromide (HBr), or from many solid metal bromides (MBr₂), (reaction 1). The facile reaction of methane with bromine then forms methyl bromide and hydrogen bromide under modest conditions, which can be subsequently reacted over zeolites to produce coupled higher molecular weight hydrocarbon products and additional HBr, (reaction 2). The chemistry of methyl bromide coupling is analogous to methanol coupling; zeolite catalysts have been used to produce olefins and/or aromatic products (-(CH₂)-) in approximately the same distributions as observed from methanol coupling [10, 11]. To regenerate bromine, one process option is to react the hydrogen bromide co-product with the metal oxide (MO), produced in reaction 1, to regenerate the metal bromide (reaction 3), such that the overall reaction is partial oxidation of methane, with hydrogen going to water (reaction 4).

Here -(CH₂)- indicates a mixture of hydrocarbons. The overall process is potentially simpler than synthesis gas-based alternatives and has no CO₂ release because oxygen and carbon are never in direct contact. However, the halogen-based process suffers from the need to separate and recycle stoichiometric amounts of bromine. The necessary unit operations for heat transfer and separation of large mass flows of corrosive chemical species is costly when traditional heat exchangers and separations are utilized. A particular challenge is the separation of HBr from light alkanes and heat management of the exothermic HBr oxidation [12]. Modifications to the process employing oxybromination have faced similar challenges [13-16]. A continuous process approach to separation of HBr, and regeneration of bromine using a regenerable solid metal oxide in a switched-bed zone reactor, has been proposed [17]. Unfortunately, the large lattice size change associated with the solid oxide-to-bromide cycle

limits lifetime, cycleability, and the regenerable bromine capacity of the solid reactants. Further, in solid-based systems, reaction of hydrocarbons with solids decreases carbon yields and necessitates separation of HBr from the hydrocarbons prior to reaction with the solids.

HBr oxidation in aqueous solutions of metal hydroxides has also been used for HBr oxidation in a chemical looping process [18]; however, the halogenation and oligomerization reactions proceed at different temperatures. Further, high steam pressure is required to maintain the metal hydrates, which may have limited adoption of this method [19]. Molten halide salts have been used in halogen-based hydrocarbon reactions. For example, molten iodide salts have been used as a source of iodine by reaction with oxygen in oxidative dehydrogenation [20-22]; the produced oxide or hydroxide reacts with hydrogen iodide to regenerate the molten iodide salt. Iron chlorides have also been used for the chlorination of hydrocarbons [18]. Molten salts as catalysts on solid supports have demonstrated longevity in applications that include the Deacon Process [23], which use supported molten copper chloride for HCl oxidation.

In this work, we explore the use of a regenerable molten salt-based chemical looping cycle as a reactive separation, as schematically shown in Figure 1, to avoid the limitations of previously-proposed halogen-based GTL processes.

Figure 1. Process configuration based on a molten salt chemical looping cycle with reactive separation of HBr. MBr is a liquid halide salt and MO is a solid oxide suspended in a halide salt melt. -(CH₂)- indicates a mixture of hydrocarbons

Molecular bromine and suspended solid metal oxides are generated from the oxidation of the bromide salt. This occurs at the temperature required for subsequent methane activation and conversion to higher molecular weight products. The formation of methyl bromide and its subsequent conversion to hydrocarbon products is well known. The hydrocarbon products and HBr are then contacted with the metal oxide suspension in the molten salt, reacting away the HBr, leaving steam and hydrocarbons for final separation. There is no need to ever cool or

compress the streams containing bromine for separation. In this work, we address the following questions to realize reactive separation of HBr using molten-salt based chemical looping:

- i) Which metal oxide/bromide combinations have favorable thermochemical properties for chemical looping between the oxide and bromide (reactions 1 and 3) below 450 °C?
- ii) When mixed with an inactive molten salt carrier, what are the rates of reaction and the stable, regenerable bromide capacity of the mixture?
- iii) What are the relative rates of HBr and hydrocarbon oxidation with a metal oxide, and how do they change when the oxide is suspended in a molten salt?
- iv) What improvements to existing bromine-based GTL processes are possible using molten salt-based reactive separation?

The thermochemistry of a variety of oxide-bromide combinations were examined and nickel was found to have favorable properties as an oxide and as a bromide. Using the low melting point eutectic salt (KBr-LiBr) as a “solvent”, nickel bromide/oxide was investigated in fixed bed reactors and bubble columns. Based on the laboratory data, a conceptual process model was created in ASPEN Plus, allowing comparison to be made to existing and alternative processes.

2. Experimental

2.1 Selection of Halide/Oxide Combinations

The Gibbs free energy of the metal halide oxidation reaction (reaction 1) and the metal oxide halogenation reaction (reaction 3) were evaluated using standard databases and software tools[24]. We examined bromides, chlorides, and iodides. Stable halides and oxides of a variety of metals were screened based on whether or not the free energy of both reactions 1 and 3 were negative. The screen was conducted for temperatures at or near the reaction temperatures for methane conversion chemistry, reaction 2. The thermodynamic calculations were done at 500 °C. Sufficient thermochemical data was available for 68 oxide/halide, hydroxide/halide, oxyhalide/halide, and oxide/oxyhalide pairs to chlorine, bromine, and iodine using the following cations: aluminum, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, calcium, cerium, cesium, chromium, cobalt, copper, dysprosium, erbium, europium, gadolinium, gallium, germanium, gold, hafnium, holmium, indium, iridium, iron, lanthanum, lead, lithium, lutetium, magnesium, manganese, mercury, molybdenum, neodymium, nickel, niobium, osmium, palladium, phosphorus, platinum, potassium, praseodymium, rhenium, rhodium, rubidium, ruthenium, samarium, scandium, selenium, silicon, silver, sodium, strontium, sulfur, tantalum, tellurium, terbium, thallium, thulium, tin, titanium, tungsten, vanadium, ytterbium, yttrium, zinc, and zirconium.

2.2 Activity Screening of Salts

Solid bromide salts of candidate materials (0.25 grams) were placed in ¼” diameter quartz tubes and heated to 500 °C in oxygen. Bromine was readily observed visually and only candidates that were highly active for bromine generation were retained for further study. Active candidates were defined to be those that evolved observable bromine upon contacting with oxygen at or below 500 °C. The samples were maintained at temperature until bromine was no longer observed. The samples were then cooled to 400 °C, and 5 ml of liquid hydrobromic acid (48 wt % in water) was delivered using a syringe pump and subsequently vaporized upon

entering the sample tube. After purging with argon and reheating to 500 °C, the sample was again exposed to oxygen, and if bromine was eluted, the bromide salt must have been regenerated. Previous work suggested that some bromides show different reactivity after one complete cycle, so each candidate was cycled twice to determine the light off temperature and whether it could be regenerated at 400 °C.

2.3 Molten Salt Preparation and Cycling

NiBr₂ (>99.99% trace metals basis, Sigma-Aldrich) was combined with a KBr-LiBr (>99.99% trace metals basis, Sigma-Aldrich) prepared at the eutectic point (60 mole % LiBr, 40 mole % KBr) and the mixture heated in a quartz vessel using a burner. The solution was heated slowly in argon to drive off excess water, until a uniform melt was observed. The mixture was further dried by sparging with argon for approximately one hour. The KBr-LiBr eutectic melts at 350 °C. The melting temperature of the ternary mixture increased to 450 °C when 20 mole % NiBr₂ was added. The molten salt mixture was cycled in two different configurations: (i) in a homogeneous melt with gas contact by sparging, and (ii) by supporting the molten salt on solid silica in a packed bed reactor.

Mixtures of solid salts were heated under a nitrogen atmosphere with a gas burner in 19 mm diam. x 150 mm long quartz tubes. Dehydration occurred and temperatures were maintained until a homogeneous melt formed, filling approximately 50% of the tube volume. The tube was then placed in a cylindrical heating block after the salt was melted. A 3 mm diameter quartz tube was inserted concentrically into the melt for gas sparging, and it was found that reactors with diameters large enough to allow a pathway for suspended oxide particles to circulate were suitable for cycling. Too small a reactor diameter resulted in “bubble lift” of the particles to the surface of the melt and the formation of an aggregate plug.

The sparged gas exited the tube headspace after flowing through the salt and was sampled at a Hastalloy junction through a glass capillary (80 micrometer diameter) to a mass spectrometer (SRS RGA 300). All connections between the reactor and mass spectrometer were heated to 125 °C to prevent condensation. When a packed bed was employed, the lines to the mass spectrometer were the same; however, a 1.25 cm diameter quartz tube in a steel heating block was used and quartz wool held up the solid catalyst. The small size of the reactor limited residence times to under 1 second.

To allow more rapid cycling of the salt mixture, the salt was supported on silica by dissolving a 0.2:0.48:0.32 molar ratio of NiBr₂:LiBr:KBr in water with 80 mole % Davicat SI 1102 silica and dried at 100 °C for 12 hours. After drying, the supported salt was heated in argon to 850 °C with a torch, melting the salt. When NiBr₂ was used alone, the same procedure was followed using the same number of moles of NiBr₂.

2.4 Conceptual Process Modeling

To examine the potential process benefits of reactive separation using molten salt chemical looping, a conceptual process model was developed using Aspen Plus V8.6. The PSRK property method was used, as it contains a suitable thermodynamic package for mixtures of non-polar and polar components in light gases above an operating pressure of 10 bar. The indirect oxidation process enables the heat of the three exothermic reactions to be managed more effectively and eliminates the heating and cooling steps between the main reactors. The process includes a methane bromination reactor, a methyl bromide oligomerization reactor, and molten salt reactors for HBr separation and oxidation. In the bromination step, methane and bromine are

fed to the bromination reactor in a ratio of 1.25:1 with complete conversion of bromine. The coupling reactor assumes 100% conversion of alkyl bromides to heavier hydrocarbons (alkanes, alkenes and aromatic components). The product mixture (HBr in a mixture of hydrocarbons) is then sent to the molten salt looping section containing the NiO solid suspension where it is assumed that 100% HBr conversion occurs to produce steam, with the hydrocarbon mixture unchanged. The NiBr₂ is then oxidized, with complete conversion of oxygen, in the molten bromide salt looping section. The RadFrac unit operation was applied to model the hydrocarbon separation because it is well-suited for the modeling of multistage vapor/liquid fractionation operations. This module is also suitable for narrow and wide boiling range system, especially for non-ideal liquid phase modeling.

3. Results and Discussion

3.1 Selection of Halide/Oxide Combinations

The thermochemistry of 68 metal halide/oxide pairs was examined, and 27 cations were found to have negative reaction free energies at 500 °C for both reactions (1) and (3) with stoichiometric reactants. Figure 2 lists the candidates, 19 of which are within the top left circle, which indicates that those compounds complete reactions (1) and (3) when bromine is the halogen. Similar assessments were performed for the chloride and iodide systems. Hydroxide and oxyhalide formation was also taken into account. Other factors involved in the salt selection included volatility, stability against hydrolysis, and redox activity. The screening results are listed in Table 1.

Figure 2. Cations with negative Gibbs free energies for both oxidation of the metal halide and halogenation of the metal oxide at 500 °C are listed. The bromine circle represents metal bromides that meet two criteria: (1) The reaction between the metal bromide and oxygen and (2) the reaction between the metal oxide and HBr proceed spontaneously (i.e. have negative reaction free energy). The figure also represents the results of iodide-oxide and chloride-oxide couples.

After thermochemical screening, appropriate salts for chemical looping were further screened based on physical and chemical properties. To facilitate transport and insure

regenerability, the molten bromide must be a liquid or solid slurry in an inert salt, the bromide must react with oxygen at a reaction temperature of less than 500 °C, and the oxide must react with HBr at similar temperatures. We eliminated oxides that reacted with HBr to make Br₂ (which is common for salts with cations that have multiple accessible oxidation states), for two reasons: (a) Br₂ should not be released into downstream equipment; (b) Br₂ would react with hydrocarbons. Additionally, salts that were extremely expensive were excluded. The screen pointed to two suitable candidate cations: magnesium and nickel. Magnesium bromide was studied; however, high conversion of HBr was not possible below 500 °C due to the hydrolysis of MgBr₂. With all these criteria in mind, nickel bromide was selected as the best candidate for a regenerable salt.

Table 1. Cations with favorable thermodynamics for the two reactions considered in a bromine system (reactions 1 and 2). Reasons for considering or not considering the system are also listed.

Element	Reason for Elimination
As	AsBr ₃ boils at 221 °C
Bi	BiBr ₃ boils at 462 °C and did not react with O ₂ at 450 °C
Co	CoBr ₂ did not react with O ₂ at 500 °C
Eu	Expensive
Gd	GdBr ₃ did not react with O ₂ at 500 °C
Ge	GeBr ₄ boils at 186 °C
In	InBr ₃ did not react with O ₂ at 500 °C
Ir	Expensive
Fe	Releases Br ₂ upon addition of HBr
La	LaBr ₃ did not react with O ₂ at 500 °C
Mg	Equilibrium conversion less than 90 %
Mn	Releases Br ₂ upon addition of HBr
Nd	Nd ₂ O ₃ did not react with HBr at 500 °C
Ni	CANDIDATE
Pr	Releases Br ₂ upon addition of HBr
Te	TeBr ₄ boils at 421 °C
Sb	SbBr ₃ boils at 288 °C
Sn	SnBr ₄ boils at 205 °C
Zn	ZnBr ₂ did not react with O ₂ at 500 °C

KBr-LiBr was chosen as a carrier salt because it is the lowest melting bromide salt mixture that does not react in any part of our system. The salt is stable in the presence of oxygen and hydrogen bromide at the reaction conditions. A low melting point of the base salt allowed for a relatively high amount of NiBr₂ to be added without forming a solid phase. No solids were predicted to form in the bromide salt based on the thermodynamics. In addition, KBr-LiBr is relatively inexpensive and innocuous, so other carrier salts were not investigated.

3.2 Material Cycling in a Bubble Column

Molten salt mixtures ($\text{NiBr}_2\text{-KBr-LiBr}$) were reacted with gas phase reactants in a bubble column and the product stream monitored by mass spectrometry. The partial pressures of the product gases and unreacted feed gases in the stream exiting the bubble column, relative to the argon carrier gas, are shown in Figure 3.

Figure 3. Relative partial pressures of products from two cycles. (a) The products of the reaction $\text{NiBr}_2 + \text{O}_2 \rightarrow \text{NiO} + \text{Br}_2$ performed as follows: 5 sccm Ar : 10 sccm O_2 were introduced into a differential bubble column containing 60 grams $\text{NiBr}_2\text{-KBr-LiBr}$ molten salt mixture. (b) In the second half-cycle the reactor was purged with Ar after which 5 sccm Ar : 14 sccm HBr were introduced into the slurry formed in the first cycle (which contained the suspension of NiO powder produced in (a) in molten $\text{NiBr}_2\text{-KBr-LiBr}$). The products of the reaction $\text{NiO} + 2\text{HBr} \rightarrow \text{NiBr}_2 + \text{H}_2\text{O}$ (the second half-cycle) in a differential bubble column with residence times of 1 second are shown. Data shown in both (a) and (b) was taken in the third complete cycle of the process.

Oxygen conversion was measured at different temperatures. Prior work in cycled solid oxide-bromide [6] showed that converting, multiple times, a solid oxide to a solid bromide results in the cracking of the solid particles and the formation of a fine powder which can then be entrained by the gas flow. This is not a problem for the present process since we cycle from fine solid NiO powder suspended into molten KBr-LiBr, to NiBr_2 which dissolves in the melt. Thus we cycle a solid to liquid and back and cracking of the solid particles is no longer an issue. To show this we cycled the dissolved NiBr_2 to NiO back-and-forth two times by reaction with oxygen and HBr, before collecting the data reported in Figure 3. The bromide melt, which contained 20 mole % NiBr_2 in KBr-LiBr, reacted with oxygen flowing at 10 sccm at 500 $^{\circ}\text{C}$. The bubble residence time in the melt was less than 1 second and the conversion of oxygen was 13% at 500 $^{\circ}\text{C}$ and 25% at 600 $^{\circ}\text{C}$.

When studying the oxidation of liquid NiBr_2 to solid NiO using oxygen, we found that two factors control the conversion. First, oxygen conversion was controlled by the flow rate (Supplementary Material, Figure S1). In a bubble column, the flow rate changes the rate at which bubbles of a fixed size leave the orifice through which they are introduced, but the bubble rises at a velocity that is determined by the relative densities and the height of the liquid column

(i.e., not by the gas flow rate). The significant change in conversion that was observed for relatively small flow rate changes may be due to the fact that there is a difference in oxygen contact time with the salt, which depends on the gas flow rate during bubble formation. If the oxygen bubble is formed more slowly, the oxygen-salt contact time will be longer, even if the time spent rising through the melt is fixed. Secondly, oxygen conversion was observed to be temperature dependent (Figure S1). We believe this dependence arises because the reaction occurs at the gas-salt interface.

It was seen that 15% of the NiBr_2 in the molten salt mixture was converted by O_2 to solid suspended NiO particles in the first half cycle. In the second half of the chemical looping cycle, suspended NiO was contacted in the bubble column with HBr at 500 °C (Figure 3, b). HBr conversion and H_2O formation were observed. As the concentration of oxide particles decreased, the rate of the HBr reaction decreased. The total water produced was determined and is consistent with 100% conversion of NiO to NiBr_2 . In the size-limited experimental set-up, the suspended NiO was dispersed, but observed to be in qualitatively higher concentrations at the bottom of the reactor tube. NiO in unmixed suspension settled to the bottom; however, sparged reactant gases readily suspended the small particles.

The regenerable bromine content per unit reactor volume was calculated from the data. When 0.185 g of 20 mole% NiBr_2 , dissolved in a KBr-LiBr eutectic, reacted with O_2 , 100% of the NiBr_2 was converted to NiO at 500 °C. We also observed that 100% of the NiO was converted to NiBr_2 when NiO was suspended in KBr-LiBr and HBr was bubbled through. Using the measured density of the bromide salt (without gases bubbling) and experimental results with extremely short residence times, the regenerable bromine content was ~ 4000 moles Br_2/m^3 salt.

3.3 Packed Bed Reactor

The NiBr_2 -KBr-LiBr salt mixture was supported on SiO_2 to allow more rapid cycling of the small bromide reservoir, and enable a direct comparison with supported NiBr_2 solid. A typical cycle is shown in Figure 4, and the results from 25 cycles (Figure 5) suggest that there is initial deactivation, followed by stable cycling. Phase segregation on the support may cause the deactivation; this is supported by SEM images taken after reaction which show small clusters as well as large plates present on the surface, each with different elemental compositions (Supplementary Material, Figure S2).

The rate of HBr oxidation by NiO was much faster than the rate of O_2 consumption by NiBr_2 at 500 °C. The rate of HBr reacting with NiO is fast enough that 100% HBr conversion was obtained in a total time of 3 seconds. A half-cycle (Figure 4, b) consisted of HBr introduction to NiO at 500 °C, followed by complete HBr conversion and corresponding water production for 20 minutes. The abrupt drop off of the water trace and the simultaneous increase in the HBr trace are associated with complete conversion of NiO to NiBr_2 . The integral of the water signal is indicative of NiO conversion. Oxygen was then introduced and the integral of the bromine signal was used to quantify the amount of NiBr_2 converted.

Figure 4. Representative cycle between nickel oxide and nickel bromide using HBr and O_2 on supported $NiBr_2$ -KBr-LiBr salt. 1 gram of SiO_2 with 20 mole % $NiBr_2$ was reacted with (a) 10 sccm O_2 and 5 sccm Ar. In (b), the resulting solid from (a) was reacted with 1 sccm HBr and 5 sccm Ar.

Repeated cycles (Figure 5) were performed using the same procedure described for the experiment in Figure 4. When oxygen was first introduced, 100 % of the $NiBr_2$ was converted to oxide using the supported salt; however, after 3 half-cycles, the conversion dropped to 65% and remained stable for 25 more half-cycles. Pure $NiBr_2$ (without KBr-LiBr to make a melt) was supported on the same SiO_2 used for the supported melt, and at the same loading for comparison under the same reactor conditions. Initial deactivation was also observed for pure solid $NiBr_2$, and repeated cycling at 40% capacity was observed. More nickel was used per cycle when supported as melt than as a solid; in fact, 50% more nickel cycled when nickel bromide was dissolved in a supported salt.

Incomplete conversion of nickel is likely due to regions where reactants cannot access the NiO or $NiBr_2$, and we hypothesize that some of this is due to a layer of surface bromination or oxidation that prevents diffusion of the reactants into a particle core. When nickel bromide is dissolved in another salt, the NiO falls out into solution when it is formed. When nickel oxide is brominated in the salt, the bromide layer dissolves in the salt and allows for further bromination. When using the supported molten salt, incomplete nickel conversion may be attributed to phase segregation on the support, which is consistent with a higher initial drop in activity.

Figure 5. (a) $\text{NiBr}_2\text{-NiO-LiBr-KBr}(l)$ was supported on SiO_2 and reacted with cycles of O_2 (blue) and HBr (green) at $500\text{ }^\circ\text{C}$. The integral of the Br_2 signal was used to calculate the amount of nickel cycled from bromide to oxide, and the integral of the H_2O peak was used to calculate the nickel cycled from oxide to bromide. In (b), the same conditions were used for $\text{NiBr}_2(s)$ supported on SiO_2 . In both cases, 20 mole % nickel on silica was used.

The surface of the supported mixed salt was not uniform and the lack of a well-mixed uniform layer was likely a contributing factor to incomplete conversion of nickel during every cycle. This was supported by the fact that SEM images showed many different surface structures on the mixed salt surface after reaction (Supplementary Material, Figure S2). Overlapping plates stretching 10-100 microns were present on much of the mixed salt surface, which suggested melted areas during reaction; however, many areas had small clusters that did not appear to have melted. In addition, the BET surface area of the supported mixed salt was significantly lower than either the area before reaction or the area of nickel bromide supported salt (Supplementary Material, Table S1), suggesting that many of the pores were filled with molten salt; however, the area was higher than if the entire surface was smoothly and uniformly covered.

The limitations of supported molten salts are eliminated in the proposed circulating molten salt chemical looping scheme because the oxide particles are continuously restored to the homogeneous melt, essentially resetting the crystalline lattice every cycle. Further, a supported bromide would have a regenerable bromine capacity much too small for a viable commercial process. Even with the short residence times used in our lab-scale reactors, the 4000 moles Br_2/m^3 reactor found in the bubble column is far greater than the 345 moles Br_2/m^3 available, even at 100% conversion, from the supported material. Further, it is unlikely that either the supported molten salt or supported solid would have sufficient long-term stability.

3.4 Hydrocarbon Oxidation

In the methane conversion process outlined, HBr is to be separated from a product stream of alkanes, alkenes, and aromatic hydrocarbons at $500\text{ }^\circ\text{C}$ by selectively reacting with a metal oxide, leaving the desirable hydrocarbon products unreacted. We selected propylene as a model hydrocarbon to compare the relative rates of reaction between HBr and the expected hydrocarbon products of methylbromide oligomerization. In a control experiment, propylene was passed over supported solid NiO , that had been produced by oxidizing supported NiBr_2 in air, to determine how propylene reacts with NiO . When C_3H_6 was contacted with NiO , high conversion to carbon oxides was observed, as expected; there was less carbon in the effluent than in the feed which suggests significant coking (Figure 6), which was more prevalent on the reduced nickel oxide. This experiment was also repeated with ethylene and benzene in place of

propylene. Ethylene and benzene were observed to react and form carbon oxides at 450 °C and 545 °C, respectively.

Figure 6. Mass spectrometry traces of reactor effluent when propylene is partially oxidized by solid NiO in a packed bed reactor. 1.6 sccm argon was flowed with 0.12 sccm propylene over 3 mg NiO supported on 40 mg SiO₂. The residence time was 0.85 seconds.

NiO was found to be significantly less reactive in the melt. This was tested by introducing C₃H₆ into a melt at 500 °C with suspended NiO. The NiO had been formed by bubbling oxygen through the NiBr₂-KBr-LiBr melt in the same procedure as described in Figure 2. C₃H₆ conversion of less than 1% was observed and no carbon monoxide, carbon dioxide, or methane fragments were observed by mass spectrometry in the products. When compared to an identical experiment in the NiBr₂-KBr-LiBr melt without NiO, the results were identical – less than 1% propylene conversion was observed.

HBr and C₃H₆ were then co-fed to a melt with suspended NiO, formed by bubbling oxygen through the NiBr₂-KBr-LiBr melt in the same procedure as described in Figure 2, (Figure 7). No carbon oxide products were observed. In the co-fed experiment, HBr was initially converted to water, and the conversion slowly decreased as the suspended oxide was converted to liquid bromide. The HBr conversion was the same as the instance in which C₃H₆ was absent. A small amount of hydrogen was initially produced, which correlates to 1% conversion of C₃H₆ initially, which is likely due to coking. No carbon oxides (from steam reforming or steam cracking) were observed. A small amount of hydrogen equivalent to approximately 2% of the HBr is also present in our HBr tank, which contributes to the low persistent signal observed in Figure 7.

Figure 7. HBr oxidation in $\text{NiBr}_2\text{-KBr-LiBr-NiO}$ melt in a bubble column, in the presence of propylene. At time $t = 0$ min, 13.5 sccm HBr, 4 sccm C_3H_6 and 5 sccm Ar were fed into a melt containing 60 grams on KBr-LiBr- $\text{NiBr}_2\text{-NiO}$ with suspended NiO at 500 °C that had been previously produced by bubbling oxygen through the melt.

A difference in solubility between hydrocarbons and HBr can account for the difference in reactivity between propylene and HBr bubbled through the salt with suspended oxide. Hydrocarbons are known to be very insoluble in molten halides [25]; whereas, hydrogen halides are often soluble. In order to test the solubility of HBr in molten bromide salts, a known ratio of argon:HBr was introduced into salt that was previously purged with argon. When the salt was solid (100 °C), no HBr was absorbed (see Fig. 8). Upon melting at 500 °C, the experiment was repeated. Initially, HBr was absorbed by the salt (Figure 8) until saturation, indicating that HBr is soluble in our melt at reaction temperature. When C_3H_6 was introduced to the molten salt, the response was identical to when C_3H_6 was introduced to the frozen salt, indicating there was no propylene solubility in the molten salt. As such, we conclude that HBr can readily dissolve into the salt to react with the solid suspended NiO particles, either as solvated molecular HBr or dissociated H^+ and Br^- ; whereas, olefins are unable to react with the nickel oxide because they are insoluble.

Figure 8. HBr and argon were introduced into 60 grams $\text{NiBr}_2\text{-KBr-LiBr}$ at 500 °C. The black curve represents HBr introduced to the frozen salt through solid channels at 100 °C. The red curve shows the same experiment at 500 °C, when the salt was molten. The difference between the curves represents the amount of HBr that accumulates (dissolves) when the salt is molten. For both curves, at time $t = 0$ min, 1.5 sccm HBr was introduced.

3.5 Process Considerations

A conceptual process model to produce 500 kilotons per annum (kta) of hydrocarbon product was constructed based upon experimental results (Figure 9 a) and compared to a conventional process (Figure 9 b). The cyclable liquid halide/oxide suspension allows reactive separation of HBr from a process stream containing unsaturated hydrocarbons. In both models, methane is first brominated and then methylbromide oligomerizes, and the conditions for both of these reactions are taken from the literature. HBr is then separated from the stream, either using a molten salt or conventional distillation, before HBr is regenerated back to bromine to complete the cycle. Separation of the final product stream including methane, olefins, aromatics, and water in a non-corrosive environment is not described in either model as it is well known in chemical engineering and is very similar for each case.

In both conventional and molten salt based models, methane bromination begins at 350 °C and is mildly exothermic. Preheating the methane feed is used to manage the temperature rise and 75% methane conversion is assumed in both models. The gas phase radical-mediated reaction produces a mixture of methyl bromide, di-methyl bromide, and HBr. The alkylbromide coupling reaction is also exothermic and if the outlet is too hot, coking will occur. The temperature is controlled by injecting a cooled alkane stream (C_5 in our model) upstream of the coupling reactor which also serves to react with di-methyl bromide to form methyl and propyl bromides[26]. The alkylbromides react to form higher hydrocarbons and more HBr on zeolite catalysts. The product distribution depends on the operating conditions and catalyst selected, and we chose to produce light olefins and aromatics [6, 26]. Approximately 15 MW of heat is removed from the bromination and coupling reactions to maintain the temperature of the coupling reactor products at 477 °C.

In the molten salt based process, the stream exiting the coupling reactor, containing HBr and a hydrocarbon mixture (in addition to unreacted methane), is bubbled through the molten salt with suspended NiO particles. The oxide particles react selectively with HBr to form NiBr_2 that dissolves in the melt. Approximately 200 MW of heat is generated from the $\text{HBr} + \text{NiO}$ reaction. This reactor is cooled with internal cooling coils, generating steam. In the conventional process model, the stream exiting the couple reactor is cooled and HBr is separated using corrosion resistant distillation columns, compressors, and heat exchangers. Using a water wash column has also been proposed, however it has not been used here because the model is more complex and amount of heat exchange in the presence of corrosive compounds is not significantly different. HBr is then fed into an HBr oxidation reactor where approximately 200 MW of heat is generated. Since dry HBr is much less corrosive than if water is present, the bromination and coupling reactors are run dry. Therefore, bromine and water must be cooled and separated, and re-heated before bromine is recombined with the entering methane, completing one bromine cycle.

In the molten salt system, the product stream (steam/hydrocarbon mixture without bromine) is separated and sent to the fractionation units. The liquid bromide salt mixture is

Figure 9. (a) Block process flow diagram for a process to produce 500,000 metric tons per year (500 kta) of hydrocarbon products using molten NiBr_2 experimental results from this manuscript. (b) Block process flow diagram of corrosive streams for a process to produce 500,000 metric tons per year (500 kta) of hydrocarbon products using conventional technology. In both cases,

red indicates heat exchangers heating and blue indicates heat exchangers cooling. Single lines indicate non-corrosive streams and units, and double lines indicate corrosive lines and units. Bold lines indicate inlet and outlet streams, boxes indicate reactors, ovals indicate separations, and trapezoids represent compressors.

The molten salt mixture has a high heat capacity and low vapor pressure. The high heat capacity allows the process to operate at high temperature and minimizes the coke formation by eliminating hot spots which form coke. Another process benefit is that adiabatic oxidation reactors can be used instead of isothermal reactors by applying a better heat management method to this process. Isothermal reactors are among the most expensive components of a halogen-based GTL process[27].

The biggest advantage of a molten salt process is reducing the amount of corrosion resistant heat exchange and separation units. The total heat exchange in a corrosive environment in the molten salt based process (Figure 9 a) is 205 MW, which is significantly less than the 581 MW required in the conventional process (Figure 9 b). The only separation in the molten salt process is removing HBr at 500 °C when HBr and hydrocarbons are bubbled through the molten salt. In the conventional process, the separation of HBr must be done at low temperature where HBr condenses and multiple corrosion resistant vessels and a compressor are required to remove HBr. The HBr must be re-heated to react with oxygen before being cooled again and sent to another separation vessel to remove water from HBr. In summary, we expect that the reduction of corrosion resistant heat exchangers and separation vessels using a molten salt based HBr separation process would significantly reduce the capital investment of a gas-to-liquids plant.

4. Summary and Conclusions

A molten salt chemical looping cycle was demonstrated for HBr oxidation to bromine, with reactive separation of HBr from a stream containing hydrocarbons. Based on thermochemical and physical property screening, NiBr₂/NiO was found to be a suitable salt-oxide regenerable pair for HBr oxidation and reactive separation. Reaction of O₂ with the molten bromides produces molecular bromine and a suspension of the active solid metal oxide, NiO, in an unreactive KBr-LiBr eutectic melt. The oxygen conversion at 500 °C and under 1 second residence time was greater than 10%, suggesting that with suitable reactor design and engineered gas-liquid contacting, high conversions can be realized. The HBr gas reaction rate depends on the NiO concentration in the suspension. High conversion is expected in relatively short residence times, provided a small excess of NiO is maintained in the salt.

HBr was found to have high solubility in the molten salt and propylene was found to have low solubility. The large difference in solubility of HBr and the hydrocarbons is likely responsible for the high selectivity for HBr oxidation in salt mixtures, because the molten salt covers the reactive oxide surface when it is suspended in the salt. Since the NiO is repeatedly interconverted to molten NiBr₂, long-term cycle stability is expected in bubble column type reactors. Although considerably high conversions are expected with longer residence times in scale-up, even with the very short space times used in our laboratory reactors, the regenerable bromine capacity of the looping salt was found to be ~4000 moles Br₂/m³ of total salt (0.26 kg Br₂/kg of total salt).

The selectivity to HBr in the reactive separation from a stream containing HBr and hydrocarbons is a significant improvement over past process options. This improvement allows

the bromine containing streams to be more efficiently and isothermally recycled without the need for multiple cooling and heating steps; the salt, bromine, and HBr are never cooled, reducing total heat exchange load and associated capital costs considerably. The total heat exchange in a corrosive environment in the molten salt based process was 205 MW, which is significantly less than the 581 MW required in the conventional process to produce 500 kta of hydrocarbon products. The heretofor difficult and expensive-to-manage halogen and hydrocarbon product stream has been transformed into a more convenient hydrocarbon and water stream. Relatively expensive separation operations have been replaced by potentially less expensive reactor elements.

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Works Cited

- [1] E. McFarland, Unconventional Chemistry for Unconventional Natural Gas, *Science*, 338 (2012) 340-342.
- [2] R. Horn, R. Schlögl, Methane Activation by Heterogeneous Catalysis, *Catalysis Letters*, 145 (2015) 23-39.
- [3] C. Mesters, A Selection of Recent Advances in C1 Chemistry, *Annual Review of Chemical and Biomolecular Engineering*, 7 (2016) 223-238.
- [4] D.A. Wood, C. Nwaoha, B.F. Towler, Gas-to-liquids (GTL): A review of an industry offering several routes for monetizing natural gas, *Journal of Natural Gas Science and Engineering*, 9 (2012) 196-208.
- [5] X.-P. Zhou, A. Yilmaz, G.A. Yilmaz, I.M. Lorkovic, L.E. Laverman, M. Weiss, J.H. Sherman, E.W. McFarland, G.D. Stucky, P.C. Ford, An integrated process for partial oxidation of alkanes, *Chemical Communications*, (2003) 2294-2295.
- [6] I. Lorkovic, M. Noy, M. Weiss, J. Sherman, E. McFarland, G.D. Stucky, P.C. Ford, C1 Coupling via bromine activation and tandem catalytic condensation and neutralization over CaO/zeolite composites, *Chemical Communications*, (2004) 566-567.
- [7] A. Zhang, S. Sun, Z.J.A. Komon, N. Osterwalder, S. Gadewar, P. Stoimenov, D.J. Auerbach, G.D. Stucky, E.W. McFarland, Improved light olefin yield from methyl bromide coupling over modified SAPO-34 molecular sieves, *Physical Chemistry Chemical Physics*, 13 (2011) 2550-2555.
- [8] S. Svelle, S. Aravinthan, M. Bjørgen, K.-P. Lillerud, S. Kolboe, I.M. Dahl, U. Olsbye, The methyl halide to hydrocarbon reaction over H-SAPO-34, *Journal of Catalysis*, 241 (2006) 243-254.
- [9] G.B. Kistiakowsky, E.R. Van Artsdalen, Bromination of Hydrocarbons. I. Photochemical and Thermal Bromination of Methane and Methyl Bromine. Carbon-Hydrogen Bond Strength in Methane, *The Journal of Chemical Physics*, 12 (1944) 469-478.
- [10] C.D. Chang, C.T.W. Chu, R.F. Socha, Methanol conversion to olefins over ZSM-5, *Journal of Catalysis*, 86 (1984) 289-296.

- [11] Y. Inoue, K. Nakashiro, Y. Ono, Selective conversion of methanol into aromatic hydrocarbons over silver-exchanged ZSM-5 zeolites, *Microporous Materials*, 4 (1995) 379-383.
- [12] M. Moser, L. Rodríguez-García, A.P. Amrute, J. Pérez-Ramírez, Catalytic Bromine Recovery: An Enabling Technology for Emerging Alkane Functionalization Processes, *ChemCatChem*, 5 (2013) 3520-3523.
- [13] V. Paunović, G. Zichittella, M. Moser, A.P. Amrute, J. Pérez-Ramírez, Catalyst design for natural-gas upgrading through oxybromination chemistry, *Nat Chem*, advance online publication (2016).
- [14] Z. Liu, L. Huang, W.S. Li, F. Yang, C.T. Au, X.P. Zhou, Higher hydrocarbons from methane condensation mediated by HBr, *Journal of Molecular Catalysis A: Chemical*, 273 (2007) 14-20.
- [15] F. Yang, Z. Liu, W.S. Li, T.H. Wu, X.P. Zhou, The Oxidative Bromination of Methane Over Rh/SiO₂ Catalyst, *Catalysis Letters*, 124 (2008) 226-232.
- [16] R. Lin, Y. Ding, L. Gong, W. Dong, J. Wang, T. Zhang, Efficient and stable silica-supported iron phosphate catalysts for oxidative bromination of methane, *Journal of Catalysis*, 272 (2010) 65-73.
- [17] A. Breed, M.F. Doherty, S. Gadewar, P. Grosso, I.M. Lorkovic, E.W. McFarland, M.J. Weiss, Natural gas conversion to liquid fuels in a zone reactor, *Catalysis Today*, 106 (2005) 301-304.
- [18] J. Miller, Methods for converting lower alkanes and alkanes to alcohols and diols, Patent number US5998679, Priority date 1998.
- [19] X.P. Zhou, I.M. Lorkovic, J.H. Sherman, Integrated process for synthesizing alcohols, ethers, aldehydes, and olefins from alkanes, Patent number US6713655, Priority date 2001.
- [20] I.M. Dahl, K. Grande, K.-J. Jens, E. Rytter, Å. Slagtern, Oxidative dehydrogenation of propane in lithium hydroxide/lithium iodide melts, *Applied Catalysis*, 77 (1991) 163-174.
- [21] C.T. Adams, S.G. Brandenberger, J.B. DuBois, G.S. Mill, M. Nager, D.B. Richardson, Dehydrogenation and coupling reactions in the presence of iodine and molten salt hydrogen iodide acceptors, *The Journal of Organic Chemistry*, 42 (1977) 1-6.
- [22] D.C. Upham, M.J. Gordon, H. Metiu, E.W. McFarland, Halogen-Mediated Oxidative Dehydrogenation of Propane Using Iodine or Molten Lithium Iodide, *Catalysis Letters*, 146 (2016) 744-754.
- [23] H.Y. Pan, R.G. Minet, S.W. Benson, T.T. Tsotsis, Process for Converting Hydrogen Chloride to Chlorine, *Industrial & Engineering Chemistry Research*, 33 (1994) 2996-3003.
- [24] E.B. C. W. Bale, P. Chartrand, S. A. Decterov, G. Eriksson, K. Hack, I. H. Jung, Y. B. Kang, J. Melançon, A. D. Pelton, C. Robelin and S. Petersen, *actSage Thermochemical Software and Databases - Recent Developments*, *Calphad*, 33 (2009) 295-311.
- [25] H.H. Kristoffersen, H. Metiu, Molten LiCl Layer Supported on MgO: Its Possible Role in Enhancing the Oxidative Dehydrogenation of Ethane, *The Journal of Physical Chemistry C*, 119 (2015) 8681-8691.
- [26] K. Ding, A. Zhang, G.D. Stucky, Iodine Catalyzed Propane Oxidative Dehydrogenation Using Dibromomethane as an Oxidant, *ACS Catalysis*, 2 (2012) 1049-1056.
- [27] J.P. Lange, P.J.A. Tijm, Chemical Reaction Engineering: From Fundamentals to Commercial Plants and Products Processes for converting methane to liquid fuels: Economic screening through energy management, *Chemical Engineering Science*, 51 (1996) 2379-2387.