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Feasibility study of sulfates as oxygen carriers for chemical looping processes

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ABSTRACT

The operational feasibility temperature range of chemical looping combustion (CLC) and chemical looping reforming (CLR) of the fuels methane, propane, iso-octane and ethanol was explored using the common sulphates Na_2SO_4, $CaSO_4$ and $MgSO_4$ as oxygen carriers. The chemical reaction equations for each oxygen carrier and fuel were formulated and fed into the Chemical Equations module of HSC Chemistry 5.1 software to obtain the Gibbs free energy change (ΔG) of the chemical reaction within the temperature range (200–1200°C). The CLC and CLR process operational feasibility temperature range for the fuel-oxygen carrier combination was mapped excluding the undesirable formation of SO_2 in CLC and H_2S and S in CLR. Na_2SO_4 and $CaSO_4$ were found to be suitable for all CLC and CLR systems. $MgSO_4$ was not found to be a suitable candidate for CLC or CLR processes irrespective of the fuel considered. Methane was found to be better than the other fuels studied as the operational temperature range of CLC and CLR processes were wide for all the sulphates. This short cut methodology presented in this paper can be used to predict the operational feasibility of CLC and CLR processes of different fuels and oxygen carriers.

Keywords: Chemical looping combustion, chemical looping reforming, thermodynamic study, syngas generation, oxygen carriers, sulfates

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BACKGROUND

CO_2 emission control through new processes has been widely researched to date. Chemical looping combustion (CLC) is an accepted technology to produce energy with the advantage of CO_2 separation and sequestration. Chemical looping reforming (CLR) is a technology similar to CLC, differing slightly in that it uses the minimum amount of oxygen to limit the fuel-oxygen carrier reaction to produce syngas ($H_2 + CO$) only. CLC and CLR are emerging technologies that utilize indirect combination of fuel and oxygen to produce thermal energy (CLC) or syngas (CLR). CLC and CLR have several benefits over direct oxidation such as safe indirect reaction of fuel and air using an oxygen carrier as an intermediate. Both processes are operated in fluidized bed reactor systems. The system consists of two reactors wherein fuel is oxidized by the oxygen carrier in a fuel reactor (FR) and the reduced oxygen carrier is regenerated by air in the oxidation reactor (AR). The process operates continuously and many oxygen carriers have been evaluated for long-term durability of oxidation–reduction cycles. Common fuels such as methane or petroleum coke [1] react with oxygen carriers at high temperatures (above 700°C as they are highly thermodynamically stable), to become partially oxidized (CLR-producing syngas) or completely oxidized (CLC-producing huge thermal energy). Many oxides are used in chemical looping studies of fuels.

Oxides as oxygen carriers

Inorganic oxygen containing compounds such as NiO have been used as oxygen carriers in CLC of syngas and natural gas [2], methane [3–5,15] and solid fuels [6] successfully. NiO based oxygen carriers have also been studied for CLR of waste cooking oil [7] and methane [8–16]. Cu based oxygen carriers have been studied in CLC of methane [17,22], H_2S [18], light hydrocarbons (LHC) (C_2H_6 and C_3H_8) [19], syngas [20,21] and solid fossil fuels [23,24]. CuO has also been used in CLR of syngas successfully [25]. Iron oxides have reportedly been studied for CLC of coal [26], methane [27], petroleum coke, charcoal, lignite and bituminous coals [28], solid fuels [29], natural gas [31] and coal and biomass [30]. Iron based oxygen carriers have also been studied for CLR of natural gas [32] and methane [33]. Other oxygen carriers have been used in chemical looping studies such as manganese oxides (CLC of natural gas) [34] and cerium oxide (CLR of methane) [35]. A comparison of iron, nickel, copper and manganese based oxygen carriers has been carried out for chemical-looping combustion [36]. Although metal oxides are popular as oxygen carriers, the drawbacks are their cost, their high weight/mole characteristics and some can be hazardous to the environment, which prevent their application in large-scale chemical-looping combustion systems [37]. Some transition metal oxides have more than one valancy which gives rise to unwanted byproducts in chemical looping systems. This has prompted the use of sulfates as oxygen carriers as they serve several advantages such as low cost, easy availability and superior oxygen transfer capacity [38].

Sulfates as oxygen carriers

The use of sulfates such as $BaSO_4$, $SrSO_4$ [39] and $CaSO_4$ have been reported only in CLC systems by researchers to date. Amongst these, $CaSO_4$ is the most widely used sulfate in chemical looping research studies. Zheng et al. [40] presented the thermodynamics and kinetics of $CaSO_4$ reduction with coal via a gasification intermediate in a CLC process and found that an increase in the steam/CO_2 ratio of the gasification intermediate increased the CO_2 generating efficiency and reduced the SO_2 environmental impact. Deng et al. [41] developed a reaction kinetics model of a CLC fuel reactor ($CaSO_4 + H_2$) using FLUENT, and reported a low fuel (H_2) conversion rate (34%) due to fast, large bubbles rising through the reactor, low bed temperature and large particle diameter. Shen et al. [42] studied the possibility of utilizing $CaSO_4$ as an oxygen carrier in CLC and found that the suitable temperature of the air reactor was between 1050–1150°C, while the optimal temperature of the fuel reactor was between 900–950°C. Jin et al. [43] studied the effects of partial pressure of H_2 on the performance of CLC using the reaction kinetics model of the fuel reactor $CaSO_4 + H_2$, and found that the concentration of H_2 enhanced the CLC performance. Song et al. [44] conducted a reactivity study of $CaSO_4$ in CLC of methane in a laboratory-scale fixed-bed reactor and also studied the SO_2 release behavior during reduction and oxidation. These researchers also [45] experimentally studied the CLC with $CaSO_4$ using reducing simulated coal gas, simultaneously oxidizing it back to $CaSO_4$ at 950°C in a fluidized bed reactor at atmospheric pressure, with $CaSO_4$ reactivity lasting for 15 cycles. Tian et al. [46] studied the decomposition mechanism of $CaSO_4$ in a different simulated atmosphere of CLC using a simultaneous thermal analyzer at five different heating rates. Song et al. [47] investigated the reduction kinetics of $CaSO_4$ as an oxygen carrier using the shrinking unreacted-core model and evaluated the apparent kinetic parameters of the kinetic equation that predicted the experimental data. Song et al. [48] experimentally investigated the CLC of methane with calcium sulfate and reported significant SO_2 formation at higher temperatures. No other common sulfates other than $CaSO_4$ have been used due to the problems of SO_2, S and H_2S formation in the CLC–CLR systems. Researchers are currently working on new and innovative ways of overcoming these issues. Tian et al. [49] investigated carbon deposition and sulfur evolution in the reduction of $CaSO_4$ oxygen carrier with a typical syngas using thermodynamic simulations and reported the conditions for preventing the release of sulfurous gases. Solunke et al. [50] studied the effect of H_2S from coal-derived syngas on the stability and redox kinetics of Ni- and Cu-based nanostructured oxygen carriers and reported that the carriers showed great potential for use in CLC of high-sulfur fuels.

The reactivity of the oxygen carriers differ with the fuel used in CLC and CLR processes. CLC and CLR process design requires the right compatibility of fuel and oxygen carrier. A particular oxygen carrier cannot deliver the best performance for all kinds of fuels. Hence there is a basic need to investigate the reaction compatibility of a oxygen carrier for a particular fuel in CLC or CLR processes. Such an investigation can be carried out experimentally but can prove to be costly and sometimes dangerous and therefore theoretical study is the best method to predict the fuel-oxygen carrier compatibility. Thermodynamics is the backbone for process development. Gibbs free energy of a chemical reaction is a fundamental thermodynamic property often used in process design, which shows the temperature (or temperature range) for reaction feasibility. This thermodynamic aspect is used in this study to design a shortcut technique to obtain process operational feasibility for the fuel-oxygen carrier combination for CLC or CLR processes. This technique works in two steps. The first step determines the temperatures for reaction feasibility (the reaction is feasible if the Gibbs free energy of the reaction is negative at that particular temperature). The second step determines process operational feasibility by limiting the temperature range to safely eliminate the feasibility of undesired by-product formation and melting of solids in the reaction system. Wider process operational feasibility temperature ranges are desirable for the fuel-oxygen carrier combination. Practical chemical reactors do not always work isothermally and wide temperature ranges can therefore help the operation of the reactor.

This paper presents a short cut technique to find operational temperature ranges of some common sulfates as oxygen carriers for different categories of fuels, which is aimed at determining the best fuel-oxygen carrier combinations avoiding undesired sulfur byproducts. Once an oxygen carrier – fuel combination obtaining a wide operational feasibility temperature range has been determined, detailed reaction feasibility studies can then be done.

METHODOLOGY

The feasibility of using Na_2SO_4, $MgSO_4$ and $CaSO_4$ as oxygen carriers for CLC and CLR reactions was explored in this paper due to their common availability, non-toxic nature and high melting temperatures (above 850°C). The common metal sulfates with their respective melting points are listed in Table 1 [51,52]. Ba, Pb and Cd compounds were neglected in this investigation as they are generally toxic and are not easily available. Complex compounds such as hydroxides, carbonates, bicarbonates of Na, Ca and Mg metals were also neglected in this investigation as they exist as stable solids at the reaction temperatures. Fuels such as CH_4 (natural gas), propane (liquefied petroleum gas), iso-octane (gasoline) and ethanol (bio-fuels) were considered in this study. The reaction feasibility was explored by using the Chemical Equations module of HSC Chemistry 5.1 software [53].

The chemical reaction equations for each oxygen carrier and fuel were formulated and fed into the software to obtain the Gibbs free energy change (ΔG) of the chemical reaction within the temperature range of 200–1200°C. The lower temperature range of 200–400°C was chosen to accommodate ethanol fuel. The feed species used for the study were sulfur, sulfate, sulfide and oxides of Na, Mg and Ca as solid and SO_2, H_2S, H_2, CO, CO_2, H_2O, CH_4, ethanol, iso-octane and propane in gaseous state. The reaction feasibility data was generated, analyzed and discussed. The feasibility study was done by plotting ΔG (kJ/mol) against reaction temperatures. The reaction feasibility in the desired direction was established for temperature ranges where the ΔG values became negative suggesting a spontaneous reaction. The melting point data of the solids involved was also taken into consideration

Table 1. **Melting point of compounds.**

Compound	Melting point (°C)
$SnSO_4$	360
$FeSO_4$	400
$Fe_2(SO_4)_3$	480
$BaSO_4$	1580
K_2SO_4	588
$CuSO_4$	600
$MnSO_4$	700
$ZnSO_4$	740
$Al_2(SO_4)_3$	770
$NiSO_4$	840
Li_2SO_4	860
$CoSO_4$	880
Na_2SO_4	884
$CdSO_4$	1000
$PbSO_4$	1170
$MgSO_4$	1185
$CaSO_4$	1450
$SrSO_4$	1580
Na_2S	1180
MgS	2000
CaS	2525
Na_2O	1132
CaO	2572
MgO	2800

to map the boundaries of reaction feasibility. The overview of CLC reactions and CLR reactions considered in this study are presented in Tables 2, 3 and 4 respectively.

The formation of undesired sulfur byproducts was taken into consideration for both CLC and CLR reaction systems. The CLC process usually uses a higher quantity of oxygen carrier to ensure the complete conversion of fuel and therefore the possibility of SO_2 formation was considered in the CLC process (Table 2, reaction 3). Similarly, in order to avoid complete conversion of fuel to CO_2 and H_2O in the CLR process, a limited amount of oxygen carrier is used, which often leads to the formation of H_2S and S in the CLR system. This point was also taken into consideration (Table 3, reactions 3 & 4). The unwanted formation of SO_2 in the CLC reaction is an oxidized state while H_2S and S are reduced states of sulfur. It is electrochemically known that H_2S on further reduction forms sulfur, it was therefore assumed that suppression of sulfur formation could be ensured by avoiding H_2S formation in CLR system. Consequently only the H_2S formation reaction (Table 3, reaction 3) was taken into further consideration when mapping the operational temperature boundary of the CLR systems. The desired process operational feasibility was established by cutting off the temperature range where the undesirable SO_2, H_2S or S products were formed and also where the solid compound melting point was exceeded. This point is explained in detail in the next section. No other reactions involving products, byproducts or inerts were considered in this study.

Table 2. **Overview of CLC reactions considered in this study.**

Fuel Reactor:	$A1\ C_mH_nO_y + B1\ M_xSO_4 = C1\ CO_2 + D1\ H_2O + E1\ M_xS$
Air Reactor:	$E1\ M_xS + F1\ O_2 = B1\ M_xSO_4$
SO_2 formation:	$A2\ C_mH_nO_y + B2\ M_xSO_4 = C2\ CO_2 + D2\ H_2O + G1\ M_xO + H1\ SO_2$

Table 3. **Overview of CLR reactions considered in this study. A1, B1, C1, D1, E1, F1, A2, B2, C2, D2, G1, H1, A3, B3, I1, J1, E2, E3, F2, B3, A4, B4, I2, J2, G2, K1, A5, B5, I3, J3, G3, L1 represent the coefficients of moles in CLC and CLR reaction schemes.**

Fuel Reactor:	$A3\ C_mH_nO_y + B3\ M_xSO_4 = I1\ CO + J1\ H_2 + E2\ M_xS$
Air Reactor:	$E3\ M_xS + F2\ O_2 = B3\ M_xSO_4$
H_2S	Formation: $A4\ C_mH_nO_y + B4\ M_xSO_4 = I2\ CO + J2\ H_2 + G2\ M_xO + K1\ H_2S$
S formation:	$A5\ C_mH_nO_y + B5\ M_xSO_4 = I3\ CO + J3\ H_2 + G3\ M_xO + L1\ S$

Table 4. Abbrevations for CLC and CLR reaction schemes in the above Tables.

Variable	Methane	Propane	Iso-octane	Ethanol
m	1	3	8	2
n	4	8	18	6
y	0	0	0	1
Na_2SO_4: M = Na, *x* = 2				
$CaSO_4$: M = Ca, *x* = 1				
$MgSO_4$: M = Mg, *x* = 1				

RESULTS

The Gibbs free energy of oxidation (regeneration) reactions of Na_2S, CaS and MgS with oxygen gave negative values (ΔG = negative) showing feasibility in the temperature range of 200–1200°C. No unwanted toxic product formation occurs in the air reactor. These factors are sufficient to establish the operational feasibility of the air reactor in the desired temperature range. Hence the air reactor operational feasibility details were not discussed in detail in this paper and the study was more focused on the operational feasibility details of the fuel reactor.

Methane

Methane is an important hydrocarbon for any reaction study. It is abundantly available as natural gas. The ΔG data of methane CLC reactions of the three sulfates (with SO_2 formation) was plotted against temperature to determine the reaction feasibility, as shown in Fig. 1. It can be seen that reactions A1 and B1 represent the CLC fuel reactor and CLC SO_2 formation reactions (explained in Table 2) for methane fuel. The Gibbs free energy reaction value for reaction A1 became negative after a temperature of 353.2°C showing its feasibility in the 353.2–1200°C range. As the melting point of Na_2SO_4 is 884°C, the temperature for the CLC operation was limited to 884°C. The Gibbs free energy value for reaction B1 did not become negative in the entire temperature range of 200–1200°C, implying that SO_2 formation did not occur in the methane–Na_2SO_4 CLC system in the desired temperature range. The methane–Na_2SO_4 CLC system is therefore technically feasible for process operation between the temperature ranges 353.2–884°C. Similarly, considering the methane–$CaSO_4$ CLC reactions (A2 and B2), it was observed that reaction A2 gave negative Gibbs free energy values from 200–1200°C, thus showing feasibility in the complete temperature range (200–1200°C). The Gibbs free energy of SO_2 formation reaction (B2) attained negative values after a temperature of 840.8°C, with feasibility in the temperature ranges 840.8–1200°C. Hence to avoid SO_2 formation, the CLC of methane–$CaSO_4$ system was operated below the temperature 840.8°C.

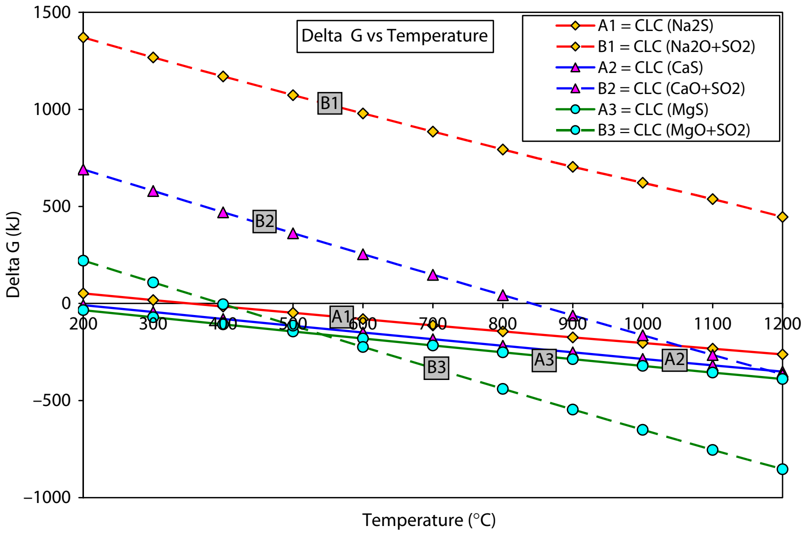

Figure. 1 CLC reactions of methane.

Thus methane–$CaSO_4$ CLC system operation showed feasibility between the temperature ranges 200–840.8°C. A similar technique was adopted for all the reaction systems and the feasible temperature ranges for operation were mapped. The methane–$MgSO_4$ CLC system showed operational feasibility between 200–400°C as SO_2 formation occurred after a temperature of 400°C. The net heat obtained from the methane CLC system was −802.56 kJ per mole of methane, which reacted irrespective of the sulfate considered. The ΔG data of methane CLR reactions of three sulfates (with H_2S formation reaction) was plotted against temperature as shown in Fig. 2. The methane–Na_2SO_4 CLR system showed operational feasibility between the temperatures 547–732.15°C and operational feasibility was also detected for the methane–$CaSO_4$ CLR system at temperatures between 487.23–520.95°C. The methane–$MgSO_4$ CLR system however did not show operational feasibility in the temperature range considered in this study as H_2S formation occurred at temperatures as low as 200°C. The net heat generated from the methane CLR system was −24.95 kJ (500°C) per mole of methane consumed for each sulfate considered generating 3 moles of syngas. All three sulfates studied were found to be good candidates for methane fuel for the CLC system. Na_2SO_4 and $CaSO_4$ were found to give the most wide operational feasibility temperature ranges for methane CLC and CLR systems respectively. The methane–$CaSO_4$ system was found to have the widest operational temperature feasibility range for the CLC system, while methane–Na_2SO_4 combination gave the widest operational temperature range (547–732.15°C) for CLR.

Propane

Propane is a major constituent of liquefied petroleum gas (LPG), which is naturally available worldwide. Figure 3 shows the ΔG data plotted against temperature for propane CLC reactions (with SO_2 formation reaction) for the three sulfates. The propane–Na_2SO_4 CLC system showed operational feasibility between 238.71–884°C, the propane–$CaSO_4$ CLC system (also separately studied [54]) showed operational feasibility between 200–782.8°C while the propane–$MgSO_4$ CLC system showed operational feasibility between 200–357.69°C, without the problem of SO_2 formation. The net heat obtained from the propane CLC system was found to be −2043.97 kJ heat per mole of propane consumed irrespective of the sulfate considered. The ΔG (kJ) data of propane CLR reactions of the three sulfates (with H_2S formation) was plotted against temperature as shown in Fig. 4. The propane–Na_2SO_4 CLR system showed operational feasibility between 385.46–574°C, propane–$CaSO_4$ CLR system showed operational feasibility between 329.14–368.96°C while propane–$MgSO_4$ CLR system was not operationally feasible in the temperature range considered as H_2S formation started at 200°C. The net heat generated from the propane CLR system was found to be −207.47 kJ (500°C) per mole of propane consumed for each sulfate considered, producing 7

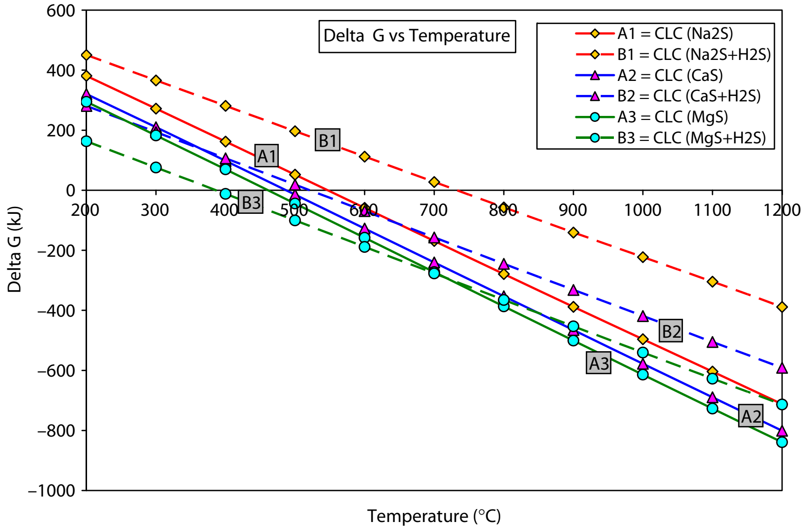

Figure. 2 CLR reactions of methane.

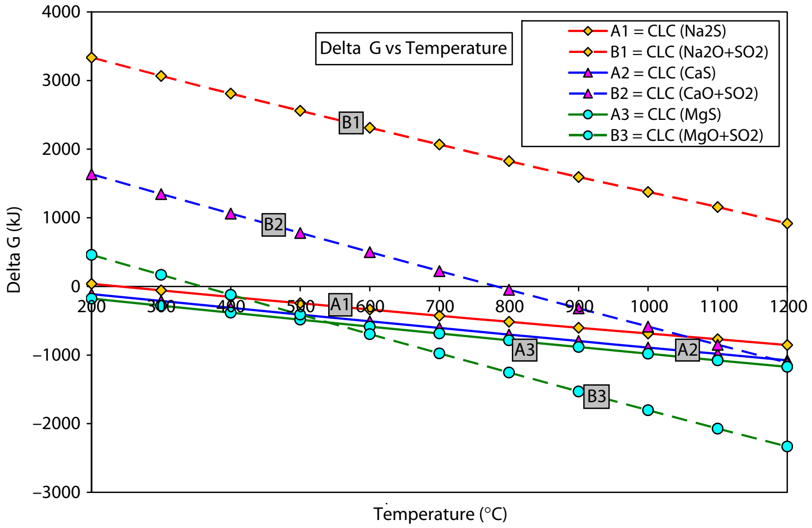

Figure. 3 CLC reactions of propane.

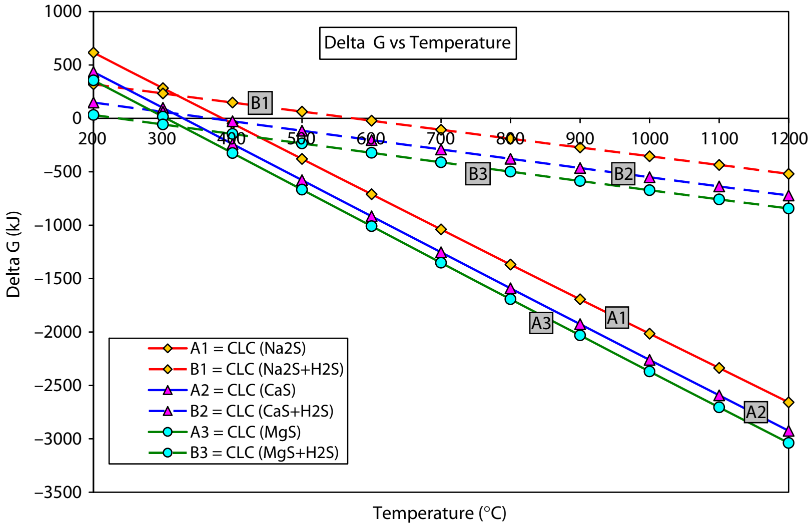

Figure. 4 CLR reactions of propane.

moles of syngas. All three sulfates showed good feasibility for propane fuel in both CLC and CLR systems except the propane–$MgSO_4$ system which was not operationally feasible in the given temperature range. $MgSO_4$ and $CaSO_4$ gave the narrowest temperature feasibility ranges for CLC (200–357.69°C) and CLR (329.14–368.96°C) systems respectively. Considering the data obtained in the study, Na_2SO_4 and $CaSO_4$ were found to be the best candidates for propane CLC system, while Na_2SO_4 was the best sulfate for the propane CLR system.

Iso-octane

Iso-octane is a popular surrogate for gasoline fuel that is easily available in almost all countries. The feasibility of iso-octane CLC reactions with the three sulfates (with SO_2 formation reaction) was investigated by plotting the reaction ΔG (kJ) against temperature (Fig. 5). The iso-octane-Na_2SO_4 CLC system showed operational feasibility between 208.76–884°C; iso-octane–$CaSO_4$ CLC system showed operational feasibility between 200–758.36°C, while iso-octane–$MgSO_4$ CLC system showed operational feasibility between 200–344.3°C, without SO_2 formation in each reaction. The net heat obtained from the iso-octane CLC system was −5101.58 kJ per mole of iso-octane used irrespective of the sulfate considered. The ΔG (kJ) data of iso-octane CLR reactions (with

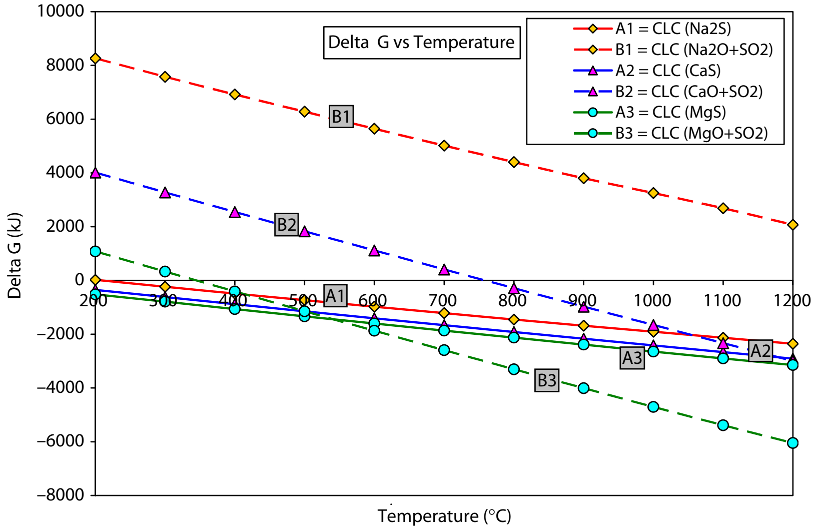

Figure. 5 CLC reactions of iso-octane.

H_2S formation reactions) of the three sulfates was plotted against temperature as shown in Fig. 6. The iso-octane–Na_2SO_4 CLR system showed operational feasibility between 339.84–525.44°C, while the iso-octane–$CaSO_4$ CLR system showed operational feasibility between 285.75–326.49°C. The iso-octane–$MgSO_4$ CLR system however was not found to be operationally feasible in the temperature range considered (200–1200°C) as H_2S formation started at 200°C. The net heat generated from the iso-octane CLR systems was found to be −626 kJ (500°C) per mole of iso-octane converted for all sulfates producing 17 moles of syngas. All three sulfates showed good feasibility for iso-octane fuel in both CLC and CLR systems except $MgSO_4$–CLR system which did not seem to be operationally feasible in the temperature range considered. $MgSO_4$ and $CaSO_4$ gave the narrowest temperature feasibility ranges for CLC and CLR systems respectively. Na_2SO_4 (208.76–884° C) and $CaSO_4$ (200–758.36°C) were found to be the best candidates for iso-octane CLC systems while Na_2SO_4 (339.84–525.44°C) was determined as the best sulfate for iso-octane CLR system.

Ethanol

Ethanol is a representative of the biofuels family. Bio-ethanol, biodiesel and many other biofuels are rapidly gaining utilization potential due to their green chemistry and current environmental pollution

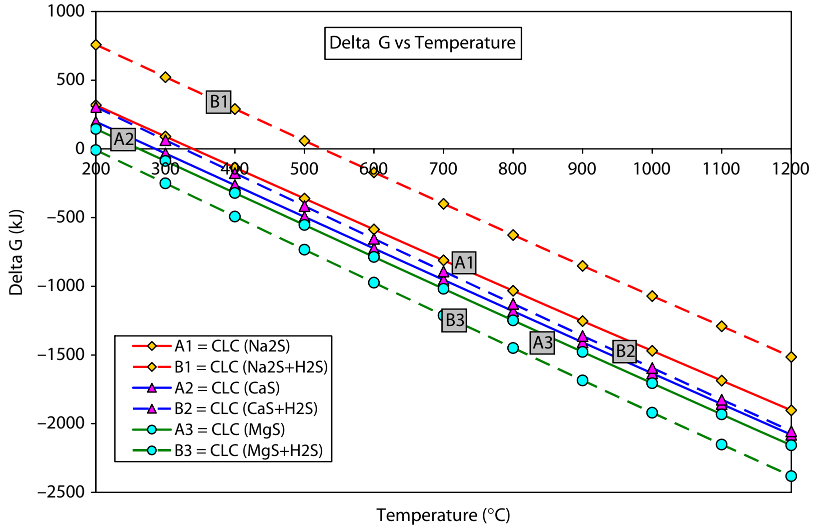

Figure. 6 CLR reactions of iso-octane.

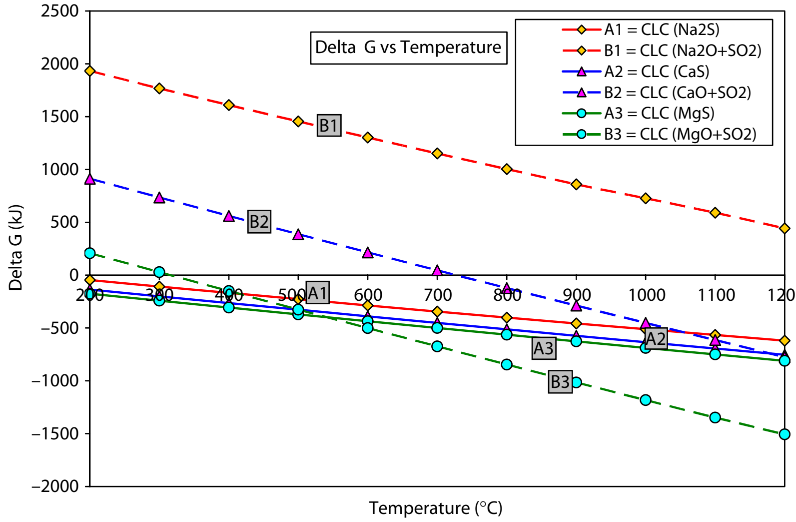

Figure. 7 **CLC reactions of ethanol.**

concerns. Depleting coal, oil and natural gas reserves, with the availability of cheap biofuels can easily make ethanol a potential fuel in future. The feasibility of ethanol CLC reactions with the three sulfates (with SO_2 formation reaction) was studied by plotting the reaction ΔG (kJ) against temperature (Fig. 7). The ethanol–Na_2SO_4 CLC system showed operational feasibility between 200–884°C; ethanol–$CaSO_4$ CLC system showed operational feasibility between 200–727.21°C, while ethanol–$MgSO_4$ CLC system showed operational feasibility between 200–315.64°C, without SO_2 formation. The net heat obtained from the ethanol CLC system was −1277.69 kJ per mole of ethanol consumed for all the sulfates considered. The ΔG (kJ) data of ethanol CLR reactions of the three sulfates (with H_2S formation reactions) was plotted against temperature as shown in Fig. 8. The ethanol–Na_2SO_4 CLR system showed operational feasibility between 265.11–368.46°C; ethanol–$CaSO_4$ CLR system showed operational feasibility between 235.88–260°C without H_2S formation, while ethanol–$MgSO_4$ CLR reaction did not show operational feasibility between 200–1200°C. The ethanol CLR system was very mildly endothermic requiring 29.54 kJ (500°C) per mole of ethanol consumed, generating 5 moles of syngas. Na_2SO_4 and $CaSO_4$ showed good operational feasibility for ethanol CLC and CLR processes, while $MgSO_4$ showed operational feasibility only for the ethanol CLC process. Na_2SO_4 and $CaSO_4$ were judged as the best candidates for ethanol CLC system, but they had very narrow temperature ranges for CLR process operation. $MgSO_4$ also showed a very narrow operational temperature range for ethanol CLC system but could not be used as an oxygen carrier in the ethanol CLR process.

DISCUSSION

The feasibility study of Na_2SO_4, $CaSO_4$ and $MgSO_4$ as suitable oxygen carriers for different categories of fuels for CLC and CLR using a short cut methodology gave some interesting results. The enthalpy of the CLC and CLR reactions depended on the fuel irrespective of the oxygen carrier used as the theoretic enthalpy of the CLC system is the same as conventional combustion (CLC merely splits the combustion reaction in two steps), but the best operational feasible temperature range depended on each fuel-oxygen carrier combination. All three sulphates were found suitable for all CLC systems but only Na_2SO_4 and $CaSO_4$ were suitable for all CLR systems. $MgSO_4$ was not found to be a suitable candidate for CLR processes irrespective of the fuel considered. $MgSO_4$–CLR system was not found operationally feasible as H_2S was produced at temperatures as low as 200°C, and although it was feasible for CLC systems, it did not have a wide enough operational feasibility temperature range compared to the other sulphates. Na_2SO_4 was found to be the best sulphate for both CLC and CLR systems for all fuels considered, with the exception of the methane–CLC system in which $CaSO_4$ had a larger operating temperature range. Na_2SO_4 CLC and CLR systems required higher temperatures than corresponding systems of $CaSO_4$ and $MgSO_4$. The use of Na_2SO_4 and $CaSO_4$ in ethanol CLR system gave very narrow operational feasibility temperature ranges and it was the only endothermic system found in this study. From the data obtained, it can be concluded that Na_2SO_4 is the best sulphate for

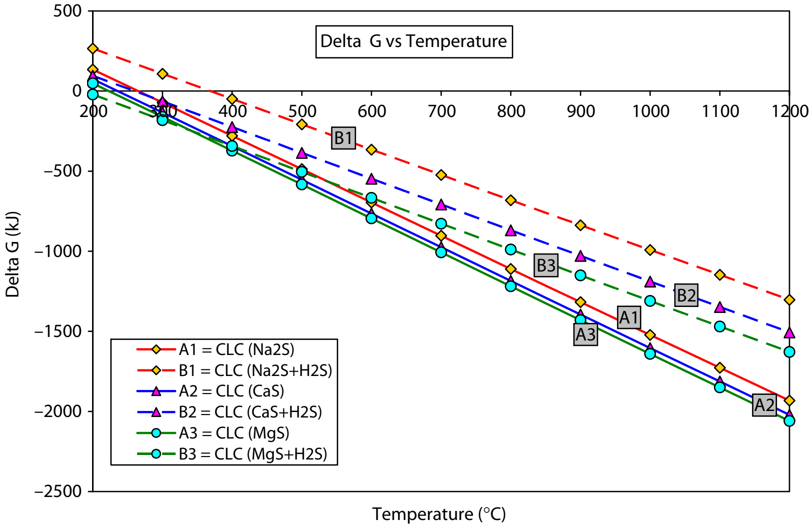

Figure. 8 CLR reactions of ethanol.

each type of hydrocarbon studied, as the formation of undesirable products i.e. SO_2, H_2S and S occurred at comparatively higher temperatures. Methane was found to be a better fuel than propane, iso-octane and ethanol as the temperature ranges of CLC and CLR operations was wider for each of the sulphates. It was also seen that the formation of $CO_2 + H_2O$ via the CLC reaction was favoured at comparatively lower temperatures than the formation of $CO + H_2$ via the CLR reaction, however the reaction enthalpy of CLC reactions was higher than corresponding CLR reactions. Iso-octane could be a good choice for the production of syngas in CLR processes as it gave 17 moles of $H_2 + CO$ per mole compared to methane (3 moles), propane (7 moles) and ethanol (5 moles) fuels. The feasibility study done by the ΔG procedure at lower temperatures (200–400°C) may need extra verification such as reaction kinetics and conversion in reactions, due to the slow nature of these types of reactions to achieve equilibrium conversions. Although this feasibility study highlights the potential of sulfates as oxygen carriers, experimental verification is also necessary to ascertain the performance of these oxygen carriers for numerous oxidation/reduction cycles in CLC and CLR processes.

CONCLUSION

The study concluded that easily and cheaply available sulphates such as $CaSO_4$ and Na_2SO_4 can serve as excellent oxygen carrier materials for chemical looping processes involving the fuels methane, propane, iso-octane and ethanol. The results of this study highlight the operating temperature ranges for CLC and CLR operations for each fuel-oxygen carrier combination. The results can be used for detailed thermodynamic modeling studies to find the maximum fuel conversions and optimum temperatures for the operation of fuel reactors. This shortcut technique study can be used for other fuel-oxygen carrier combinations to find their operating temperature ranges before investing heavily on detailed process design and experimentation.

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