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Thermodynamic Attainable Region for Direct Synthesis of Dimethyl Ether from Synthesis Gas

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Abstract**—**This paper demonstrates the use of a method of synthesizing process flowsheets using a graphical tool called the GH-plot and in particular, to look at how it can be used to compare the reactions of a combined simultaneous process with regard to their thermodynamics. The technique uses fundamental thermodynamic principles to allow the mass, energy and work balances locate the attainable region for chemical processes in a reactor. This provides guidance on what design decisions would be best suited to developing new processes that are more effective and make lower demands on raw material and energy usage.

Keywords**—**Attainable region, dimethyl ether synthesis, mass balance, optimal reaction networks.

I. INTRODUCTION

ENERGY is a fundamental element of the modern economy hence its management must be sustainable and less dependent on increasingly scarce fossil fuels. The use of energy entails substantial financial, environmental and security costs that cannot be quantified in economic terms alone. But still, customers should be able to count on a reliable supply of energy at viable prices. To achieve this, all forms of safe and reliable energy options are essential. In view of the changing climate and the decreasing availability of fossil fuels, a realistic transition to sustainable energy is required in the longer term. These calls for an international economic approach that ensures businesses and the public are not saddled with unnecessarily high costs. A viable method for reducing the cost of energy while retaining its benefits is to produce it more efficiently [1].

Industrial processes pose a serious threat to the world's natural resources for they consume them in high proportions as sources of energy for driving chemical processes that provide raw materials for many industrial chemicals. The chemical and petrochemical industries consume about 61% of global industrial energy and emit about 36% of carbon dioxide to the environment [2]. A significant portion of the energy demand is entirely for feedstock, which cannot be reduced through energy efficiency measures. The responsibility therefore for cutting back on the amount of energy needed for chemical processes rests on improving the efficiency of the processes used.

Thermodynamics has been shown to be a useful tool in studying chemical processes [3]. Its methods can be used to compare different processes [4] and also be used to understand and improve them [5]. Leonard et al. [6] presented a thermodynamic method that can be used to analyze reactions occurring in a reactor. The technique helps the design engineer know which among all the reactions happening in a reactor is/are likely to dominate in that process. It also helps the designer know the conversions and yields achievable in that particular process. This technique further makes it possible to evaluate and compare process efficiencies against their theoretical targets and allows one to identify where inefficiencies could be coming from within the process. The method can be applied to industrial processes aiming to: (1) obtain optimal results, (2) identify probable means of saving energy, and (3) devise procedures for supplying or recovering energy from the processes so as to enhance process reversibility and efficiency. The authors [6] applied this technique to the synthesis of methanol where they identified and defined the thermodynamic Attainable Region (AR).

AR provides the theoretical basis for design engineers to graphically visualise all possible concentration combinations in the solution space, which can be achieved in any chemical reaction system without restricting choices/options in an attempt to making the problem smaller. This is different from the way that reactor synthesis is often done. For instance, in the absence of theoretical tools like the AR, heuristics or "rules of thumb" are often used to limit the problem space. This approach is more of a trial and error and the trouble is that decisions are not based on science but rather on the way things have always been done [6], [7]. Not that past experience is not important or should be overlooked, but new combinations will certainly not be realised by relying only on experience and rules of thumb, and there is a potential of accidentally ruling out optimal approaches by limiting combinations of operations.

The advantage of using thermodynamic relations to analyse chemical reactions is that they do not require precise kinetic data. The relative magnitudes of the reaction rates and the range of temperatures over which these relations apply can be estimated [8], which makes thermodynamic analysis a powerful tool for process improvements and development, both for chemists as well as process and chemical reactor designers [9]. However, its greatest flaw lies in the fact that though it is exceptionally general in its applicability for solving many significant problems, it is unable to answer explicitly questions arising from the problems. For example, it can tell that a process will occur, but not how fast it will occur and as such it cannot be used alone in the determination of

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transport process or for the design of a reactor/process. Furthermore, thermodynamics does not provide the deep insight into chemical and physical phenomena that is afforded by microscopic models and theories [10].

Given a reactive system with known reactants and products, the number of possible reactions that could be employed to form desired products might be infinite, but only a few of them are realizable physically [11]. Once the stoichiometric coefficients of all the chemical species in an overall reaction are established, it is easy to determine the Gibbs free energy change and conversion ratio of raw materials to products at a specified temperature by means of mass balance calculations [12]. For an overall reaction to be thermodynamically feasible, the Gibbs free change (ΔG) must be less than zero, while that with the value of ΔG that is always greater than zero in the specified temperature range is regarded as infeasible [13]-[15].

II. DIMETHYL ETHER SYNTHESIS

Dimethyl ether (DME), also known as wood ether, methyl ether, or methyl oxide is a colorless liquid or compressed gas which has traditionally been used as a propellant in aerosols industry. Its common use is also in organic synthesis where it works as a reaction solvent for systems requiring volatile polar solvents. It is produced in a minimum of two steps. Firstly, hydrocarbons predominantly from natural gas are converted into synthesis gas (also known as syngas), a combination of carbon monoxide (CO) and hydrogen (H_2). Secondly, the synthesis gas is then transformed into DME in two different techniques. The first technique is a conventional two-step process which consists of methanol synthesis and dehydration; the second is a one-step process which directly produces DME from syngas [16]-[18].

A. Reaction Chemistry

The direct synthesis of DME from synthesis gas can be presumed to consist of the following reactions [19]:
Methanol synthesis from CO:

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H^{\circ}_{298} = -90.41 \text{ kJ mol}^{-1} \quad (1)$$

Methanol synthesis from CO_2:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H^{\circ}_{298} = -49.24 \text{ kJ mol}^{-1} \quad (2)$$

Water gas shift (WGS):

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^{\circ}_{298} = -41.17 \text{ kJ mol}^{-1} \quad (3)$$

Methanol dehydration:

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \qquad \Delta H^{\circ}_{298} = -49.24 \text{ kJ mol}^{-1} \quad (4)$$

Reactions (1)-(3) are catalysed by a methanol synthesis catalyst (either Cu or ZnO or Al_2O_3) and reaction (4) by an acidic catalyst (e.g. $\Upsilon\text{-}Al_2O_3$). Compared to the syngas-to-methanol process, these reactions form a synergistic system yielding higher syngas conversion hence greater productivity [20]. The synergy works as follows: methanol, which would otherwise be near its equilibrium value, is consumed by reaction (4), and water formed by reactions (2) and (4) is consumed by reaction (3), while reaction (3) generates Hydrogen which improves reaction (1). All these reactions are reversible and exothermic. Since (2) is merely the summation of (1), (3), this paper only considered the independent reactions (1), (3), and (4) for analysis.

III. METHODOLOGY

A. Introduction

Thermodynamics is a remarkable intellectual structure, for it deals with the scientific relationships amongst observations and is independent of the hypothetical models of the infinitesimal nature of matter; because of this independence and immediacy, it is remarkably useful. From diverse experiments (and so now from tabulated data), one can predict properties such as the direction of spontaneous chemical and physical change and the composition of reaction mixtures at equilibrium, and the response of these properties to changes in operating conditions. Hence, thermodynamic analysis if properly utilized can predict what happens in a chemical reactor. Taking into account the dependence of equilibrium conversions of chemical reactions on temperature, pressure and initial compositions, one can develop a methodology to analyse and consequently understand the performance of chemical systems [21], [22].

B. Thermodynamic Analysis of the Process

There are essentially three principles that can be used to synthesise flowsheets: these are an overall mass balance (the composition of each species in the reactor must remain positive), a constraint called the energy balance (determines heat requirements of a chemical process) and another called work/entropy balance which is associated with the ΔG of a process (the trend will always be in the direction for which $\Delta G < 0$) [6], [21], [23].

The objective in this case was to find a region where any reaction in the reactor becomes thermodynamically viable, even under altered process parameters. It is assumed that the chemical species involved in these independent reactions are completely pure and in a gas phase as shown in Fig. 1. The system was considered to be ideal hence the equations of state were used to estimate the thermodynamic properties.

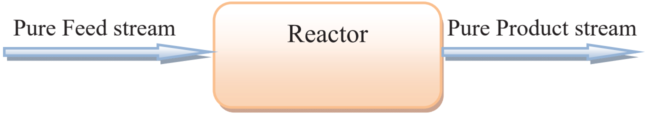

Fig. 1 Representation of this typical process showing feed and product streams

The principal idea is that the feed materials have chemical potential which based on how efficient the chemical plant is, must be conserved during the transformation of reactants into products, whether they are chemicals or direct work outputs such as electricity.

1. Temperature Dependence of Heat Capacity

The interpretation of heat as energy in transit is preceded by the idea that a body has a capacity for heat. The smaller the temperature change in a body instigated by the transfer of a given amount of heat, the greater its capacity [22]. The constant-pressure heat capacity is defined as:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{5}$$

This heat capacity relates in a simple way to a constant-pressure, closed-system process, for which (5) is equally well written as:

$$dT = C_P dT \tag{6}$$

This upon integrating leads to:

$$\Delta H = \int_{T_1}^{T_2} C_P dT \tag{7}$$

Evaluating the integral in (7) requires knowledge of how heat capacity is affected by a change in temperature and that relationship may be simplified to:

$$\Delta H = \left(C_P\right)_H \left(T - T_0\right) \tag{8}$$

2. Temperature Dependence of ΔH^0

We then treated the calculation of standard heats of reaction at different temperatures from knowledge of the value at the reference temperature of 298.15 K. The heat of reaction can be calculated as:

$$\Delta H = H_P - H_r \tag{9}$$

where: subscripts p and r represent products and reactants respectively. Differentiating (9) with respect to temperature at constant pressure:

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_P = \left(\frac{\partial H_P}{\partial T}\right)_P - \left(\frac{\partial H_r}{\partial T}\right)_P \tag{10}$$

But:

$$\left(\partial H / \partial T\right)_P = C_P$$

Therefore:

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_P = C_{P,p} - C_{P,r} = \Delta C_P \tag{11}$$

Referring to (7) and recalling (6), the standard heat of reaction can be expressed as:

$$d H_i^0 = C_{P,i^0} dT \tag{12}$$

Multiplying by the stoichiometric numbers and summing the overall products and reactants gives:

$$d \sum_i \nu_i H_i^0 = \sum_i \nu_i c_{P,i^0} dT \tag{13}$$

The term on the left side of (13) is defined as the standard heat of reaction. The standard heat capacity change of reaction is defined similarly as:

$$\Delta C_P^0 = \sum_i \nu_i c_{P,i^0} \tag{14}$$

As a result of this, the enthalpy change of a reaction (ΔH) as a function of temperature at constant pressure can subsequently be determined by:

$$\Delta H^0 = \Delta H_0^0 + \left(\Delta C_P^o\right)_H \left(T - T_0\right) \tag{15}$$

where, ΔH^0 represents the change in enthalpy at a particular temperature; ΔH$_0^0$ indicates the change in enthalpy at standard conditions (1 Bar and 25 ^{0}C); (ΔC$_p^0$)$_H$ shows the mean heat capacity as a function of temperature.

3. Temperature Dependence of ΔG^0

Before measuring the changes of ΔG as a result of changes in temperature during the course of a reaction, we must first find the relation concerning Gibbs free energy (G) and pressure. Looking first at the definition of G:

$$G = (U + PV) - TS = H - TS \tag{16}$$

Such that:

$$G = U + PV - TS \tag{17}$$

Differentiating (17) gives:

$$dG = dU + PdV + VdP - TdS - SdT \tag{18}$$

This can be simplified to:

$$\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_P = -\frac{\Delta H}{T^2} \quad \text{(Gibbs-Helmholtz)} \tag{19}$$

Interpreting and rearranging (19) gives:

$$\frac{\Delta G, T_2}{T_2} - \frac{\Delta G^0, T_1}{T_2} = \Delta H^0 \times \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{20}$$

This can also be expressed as:

$$\frac{\Delta G, T_2}{T_2} = \frac{\Delta G^0, T_1}{T_2} + \Delta H^0 \times \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{21}$$

At standard temperature and pressure, (21) makes it possible to calculate ΔG of a reaction at any temperature T_2.

4. Pressure Dependence of ΔG^0

Referring again to (18), at constant temperature:

$$dG = VdP \tag{22}$$

Partially differentiating at constant temperature gives:

$$\left(\frac{\partial G}{\partial P} \right)_T = V \tag{23}$$

For n moles of a perfect gas:

$$PV = nRT \quad 24)$$

Equation (22) then reduces to:

$$dG = nRT \frac{dP}{P} \tag{25}$$

Integrating from P_1 to P_2:

$$\Delta G = G_2 - G_1 = nRT \int_{P_1}^{P_2} \frac{dP}{P} = nRT \ln\left(\frac{P_2}{P_1} \right) \tag{26}$$

The free energy of a gas is usually related to the standard free energy G^0, which is defined as the free energy of one mole of a gas one atmospheric pressure. For standard states therefore:

$$G = G^0 + RT^0 \times \ln\left(\frac{P}{P_0^0} \right) \tag{27}$$

where G is the free energy at some pressure (P); G^0 is the free energy at a particular absolute temperature; R is the universal gas constant; T^0 is that particular absolute temperature; and P_0^0 is the standard ambient pressure.

5. Multi Reaction Stoichiometry

The general chemical reaction may be written as:

$$v_1 A_1 + v_2 A_2 + \cdots \leftrightarrow v_3 A_3 + v_4 A_4 + \cdots \tag{28}$$

where: v_i is a stoichiometric coefficient and A_i stands for a chemical formula/species. The species on the left are reactants and the ones on the right are products. The generalized stoichiometric coefficients for the above reaction may be written as:

$$\frac{dN_2}{v_2} = \frac{dN_1}{v_1} = \frac{dN_3}{v_3} = \frac{dN_4}{v_4} \tag{29}$$

With all terms being equal; a single quantity representing an amount of reaction can be used to collectively identify these terms. Thus a definition of dε is given by:

$$\frac{dN_2}{v_2} = \frac{dN_1}{v_1} = \frac{dN_3}{v_3} = \frac{dN_4}{v_4} = d\varepsilon \tag{30}$$

This can also be written as:

$$dN_i = v_i d\varepsilon \tag{31}$$

when multiple independent reactions proceed simultaneously, subscript j serves as the reaction index. A separate extent of reaction ε_j then applies to each reaction. The stoichiometric numbers are also subscripted to distinguish each species per reaction. Thus, $v_{i,j}$ designates the stoichiometric number of species i in reaction j. The fact that a number of moles of a species N_i may change because of several reactions, the general equation analogous to (31) includes a sum:

$$dN_i = \sum_j v_{i,j} d\varepsilon_j \qquad (I = 1, 2 \ldots N) \tag{32}$$

Integrating from $N_i = N_i^o$ and $\varepsilon_j = 0$ to arbitrary Ni and ε_j gives:

$$N_i = N_i^0 + \sum_j v_{i,j} d\varepsilon_j \qquad (I = 1, 2 \ldots N) \tag{33}$$

where N_i is the molar flowrate at some point in the reactor, N_i^o is the molar flowrate of the specie input to the reactor, and $v_{i,j}$ is the stoichiometric coefficients of species i in the reaction.

C. Process Mass Balance

Assuming that the system is allowed to reach equilibrium, the number of moles N_i of component i in the product stream can be obtained using the relationship between the number of moles N_i^0 of component i in the feed stream and the extent of reaction (ε) as shown by (33).

Since the requirement is a positive molar flow rate of the reactants, then:

$$N_i = N_i^0 + \sum_j v_{i,j} d\varepsilon_j \geq 0 \tag{34}$$

The inequality of all species thus determines the achievable area in the space of constraints described by the vector N, within which the system can operate thermodynamically without violating the laws governing mass balance [6].

D. Process Work and Energy Balance

Despite the fact that mass balance is such a useful tool, its aspects of the process cannot be isolated because energy and work aspects also must be considered. The energy aspects can be taken into account using an energy balance shown by (35) and the work aspect of it can be taken into account by using the Gibbs free energy balance shown by (36):

$$\Delta H_j = \left(\Sigma v_j \Delta H_{i,j}\right)_p - \left(\Sigma v_j \Delta H_{i,j}\right)_r \tag{35}$$

$$\Delta G_j = \left(\Sigma v_j \Delta G_{i,j}\right)_p - \left(\Sigma v_j \Delta G_{i,j}\right)_r \tag{36}$$

IV. RESULTS, ANALYSIS AND DISCUSSION

This section outlines the application of thermodynamic reaction equilibrium theory to the analysis of DME synthesis process. The feasibility of this process is then discussed in terms of the AR build via thermodynamic principles and graphical representations. Equations given in Section III were used to calculate the thermodynamic properties given in Table I. These properties were calculated at standard conditions with the aim of comparing them with literature before building the thermodynamic AR and the results were found to be very close to those given in [24], [25].

TABLE I
THERMODYNAMIC PROPERTIES AT STANDARD CONDITIONS

Component	**C_p [J/mol.K]**	**ΔH [J/mol]**	**ΔG [J/mol]**
H_2	28,7731	0	0
CO	29,0298	-110530	-137150
CO_2	37,0199	-393510	-394370
CH_3OH	44,2153	-200940	-162320
H_2O	33,5164	-241814	-228590
CH_3OCH_3	65,6806	-184100	-112800

1. Stoichiometric Subspace for a Single Reaction

Equation (34) provided a theoretical basis on which to build the graphical analysis. The reaction coordinate (ε) is independent of any reaction species and as such, allows for the relation between species with changing mole numbers. This can be presented as an extent plot which will eventually be interpreted in terms of a GH plot. Methanol dehydration reaction presented below will be used as an example.

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$$

We then performed the mass balance assuming the stoichiometric feed and the resulting equations are:

- For methanol (CH_3OH): $\varepsilon \leq 1$
- For DME (CH_3OCH_3): $\varepsilon \geq 0$
- For water (H_2O): $\varepsilon \geq 0$

Fig. 2 (an extent plot) is a result of the above mass balance for the three chemical species involved, where points A and B are anywhere along the extent line between the feed and products with an overall feed conversion of 40% and 80% respectively. The reaction has not yet completed at these two points hence methanol would still be expected in the reactor and would be completely converted to DME at an extent equaling 1.

2. Stoichiometric Subspace in Terms of the GH Space

The objective was to establish the performance of this system in terms of the heat and work requirements. It then became necessary to express the extent of the reactions as a function of these thermodynamic variables and this is how the resulting equations look:

$$\Delta H = \varepsilon \Delta H_f \tag{37}$$

$$\Delta G = \varepsilon \Delta G_f \tag{38}$$

where; ΔH_f and ΔG_f are the enthalpy and Gibbs free energy change of formation of a compound from its elements respectively. Critically analyzing these equations makes it clear that plotting ΔH against ΔG for each chemical species by varying ε would result in a linear relationship as shown in Fig. 3. This plot is still for methanol dehydration reaction alone.

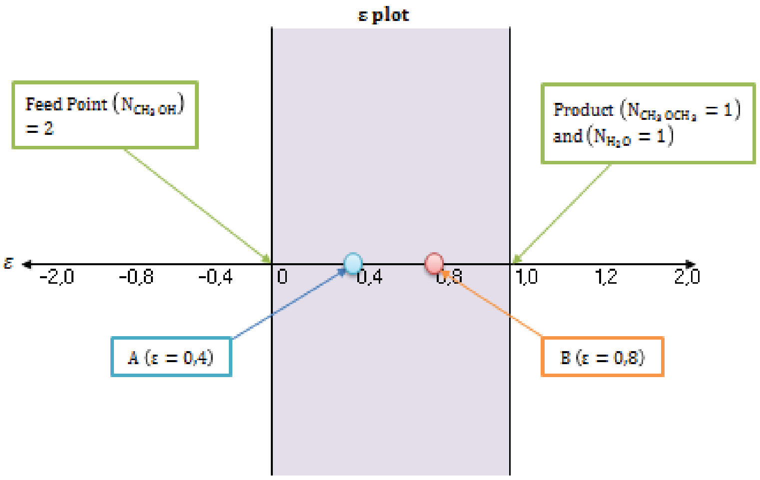

Fig. 2 An extent plot for a single reaction

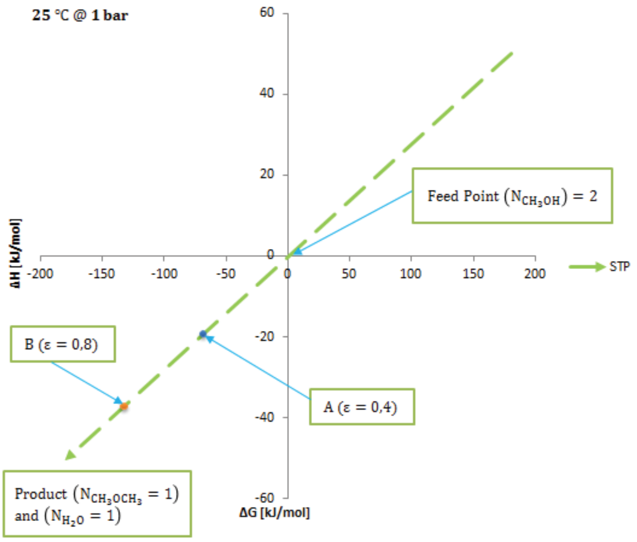

Fig. 3 GH plot for one reaction at standard conditions

3. GH Space Involving Three Reactions

We now can contemplate a more intricate case in which: (I) multiple reactions take place in a single unit (reactor) and (II) specie(s) appears in one or two chemical reactions. The reaction coordinates of these reactions can be used to compute values for ΔH and ΔG of the combined process while enthalpy and Gibbs free energy of formation are extracted from the published literature. According to Hess's law;

$$\Delta H = \varepsilon_1 \Delta H_1 + \varepsilon_2 \Delta H_2 + \varepsilon_3 \Delta H_3 \quad (39)$$

$$\Delta G = \varepsilon_1 \Delta G_1 + \varepsilon_2 \Delta G_2 + \varepsilon_3 \Delta G_3 \quad (40)$$

where, ε_1, ε_2, and ε_3 are the reaction coordinates of reactions 1, 2, and 3; ΔH_1, ΔH_2, ΔH_3, ΔG_1, ΔG_2 and ΔG_3 are the enthalpy and Gibbs free energies of reactions (1), (2) and (3) respectively; and ΔH and ΔG are the enthalpy and Gibbs free energy of the combined process. In an attempt to ascertain the performance of both reactants and product species during this synthesis, we now consider the graphical technique to analyse these concurrent reactions, where we chose −2 to +2 as the reaction coordinates.

Eliminating ε_1 and ε_2, and ε_3 and N_i for each species (CO, CO_2, H_2, H_2O, CH_3OH and CH_3OCH_3) in terms of the overall ΔH and ΔG allows for plotting a linear relationship that would meet the reactor's AR as shown in Fig. 4. This diagram represents the performance for a feed of CO (2 mols), CO_2 (1 mol), H_2 (3 mols), H_2O (0.5 mol), and CH_3OH (2 mols) at ambient conditions. The shaded region is the area where there are feasible reactions because the conditions required to optimize the process in a steady state system are satisfied and all the species are positive.

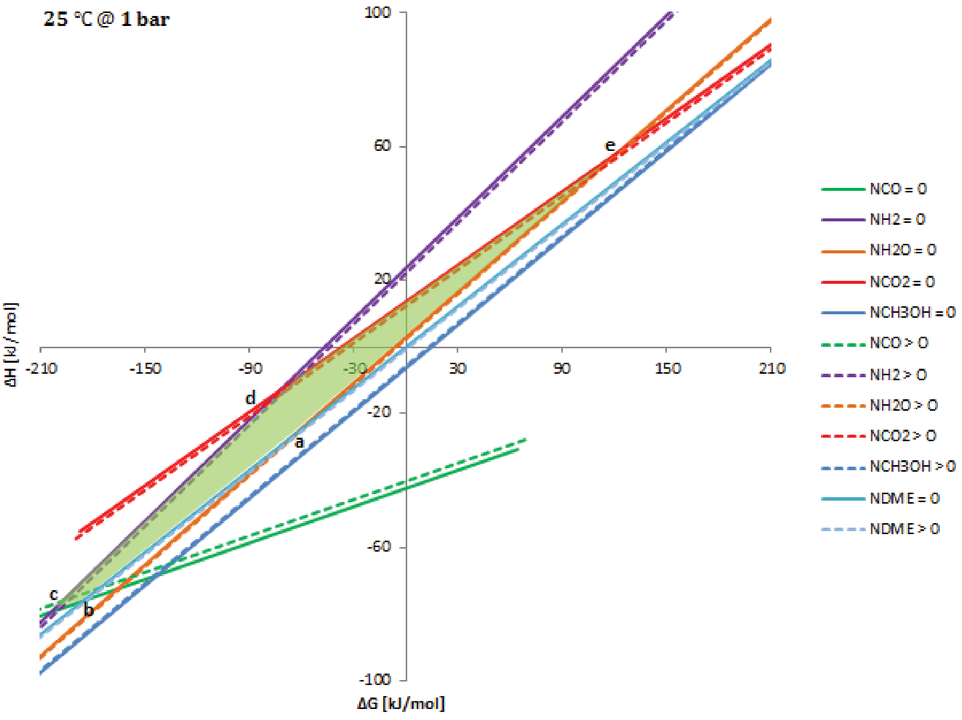

Fig. 4 AR for the reactor

Looking at the boundaries of Fig. 4, solving for reaction extents and substituting the results into the general equations (1)-(3) lead to the following overall reactions:

Between points a and b (the N_{DME} = 0 line), methanol is produced via the hydrogenation of Carbon monoxide in the presence of water as:

$$3CO + 3H_2 + H_20 \rightarrow 2CH_3OH + CO_2 \tag{41}$$

Between points b and c (the $N_{CO} = 0$ line), DME production begins with the general equation as:

$$3CH_3OH + 3CO + 6H_2 + CO_2 \rightarrow 3CH_3OCH_3 + 3H_2O \tag{42}$$

Between points c and d (the $N_{H2} = 0$ line), DME is produced directly from syngas and also produces carbon dioxide as shown:

$$6CO + 6H_2 \rightarrow 2CH_3OCH_3 + 2CO_2 \tag{43}$$

Between points d and e (the $N_{CO2} = 0$ line), DME is produced from synthesis gas in the presence of methanol with the general equation:

$$4CH_3OH + 2CO + 4H_2 \rightarrow 3CH_3OCH_3 + 3H_2O \tag{44}$$

V. CONCLUSION

The GH plot presented in this paper is always two dimensional irrespective of the number of reactions or species involved. This allows for easy interpretation of results which helps identify the AR and interpret its boundary in terms of the likely limiting extents of reaction.

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REFERENCES

[1] Ministry of Economic Affairs, Agriculture and Innovation. Energy Report, (2011).

[2] International Energy Agency (IEA, 2007). Tracking Industrial Energy Efficiency and CO_2 Emissions. Organisation for Economic Co-Operation and Development/ International Energy Agency (OECD/ IEA), 23-25.

[3] Patel, B., D. Hildebrandt, D. Glasser, Hausberger, B. (2005). Thermodynamics analysis of processes. 1. Implications of work integration. *Industrial & Engineering Chemistry Research*, 44, 3529-3537.

[4] Patel, B., Hildebrandt, D. & Glasser, D. (2010). An overall thermodynamic view of processes: Comparison of fuel producing processes. *Chemical Engineering Research and Design*, 88, 844-860.

[5] Hildebrandt, D., D. Glasser, B. Hausberger, Patel, B. & Glasser, B. (2009). Invited perspectives article. Producing transportation fuels with less work. *Science*, 323, 1680-1681.

[6] Leonard U. O., Hildebrandt, D., Glasser, D., & Patel, B. (2012). Attainable regions for a reactor: Application of ΔH-ΔG plot. *Chemical Engineering Research and Design*, 90, 1590-1609.

[7] Glasser, D., Hildebrandt, D. & Crow, C. A. (1987). A geometric approach to steady flow reactors: the attainable region and optimization in concentration space. *Industrial Engineering Chemical Resource*, 26, 1803-1810.

[8] Shinnar, R., & Feng, C. A. (1985). Structure of complex catalytic reactions: thermodynamic constraints in kinetic modeling and catalyst evaluation. *Industrial & engineering chemistry fundamentals*, *24*(2), 153-170.

[9] Shinnar, R. (1988). Plenary paper received too late to be included at front of issue: Thermodynamic analysis in chemical process and reactor design. *Chemical engineering science*, *43*(8), 2303-2318.

[10] Annamalai, K., Puri, I. K., & Jog, M. A. (2010). *Advanced thermodynamics engineering*. CRC Press.

[11] Lien, K., & Perris, T. (1996). Industry & academia rebuilding the partnership. *Computers & chemical engineering*, *20*, S1545-S1550.

[12] Peng, X. D., Toseland, B. A., Wang, A. W., & Parris, G. E. (1997, September). Progress in development of LPDME process: kinetics and catalysts. In *Proceedings of the Coal Liquefaction & Solid Fuels Contractors Review Conference, Pittsburgh*.

[13] Chen, L., Nolan, R., Avadhany, S., & Ghoniem, A. F. (2009). Thermodynamic analysis of coal to synthetic natural gas process. *Massachusetts Institute of Technology*.

[14] Hardiman, K. (2001). Methanol synthesis from biogas: thermodynamics, computer simulation, and economic evaluation.

[15] Li, M., Hu, S., Li, Y., & Shen, J. (2000). A hierarchical optimization method for reaction path synthesis. *Industrial & engineering chemistry research*, *39*(11), 4315-4319.

[16] Gogate, M. (1992). *A Novel Single-step Dimethyl Ether Synthesis Process from Syngas*. PhD Thesis, University of Akron.

[17] Azizi, Z., Rezaeimanesh, M., Tohidian, T., & Rahimpour, M. R. (2014). Dimethyl ether: A review of technologies and production challenges. *Chemical Engineering and Processing*, 82, 150-172.

[18] Nie, Z., Liu, H., Liu, D., Ying, W., & Fang, D. (2005). Intrinsic kinetics of dimethyl ether synthesis from syngas. *Journal of Natural Gas Chem*istry, 14, 22-28

[19] Xiao, W.D., Lu, W.Z. (2002). A novel technology of DME synthesis from syngas. *Elsevier Science Publishers B. V., Amsterdam*, 8 (1991), 279-304.

[20] Liu, L., Huang, W., Gao, Z., & Yin, L. (2010). The dehydration of methanol to dimethyl ether over novel slurry catalyst, energy sources, part A: recovery, utilization, and environmental effects. 32, 1379-1387.

[21] Smith, E. B. (1990). Basic chemical thermodynamics. 4th edition. Oxford.

[22] Smith, J. M., Van Ness, H. C., & Abbott, M. M. (2005). Introduction to chemical engineering thermodynamics. 7th ed. McGraw-Hill, New York.

[23] Warn, J. R. W., & Peters, A. P. H. (1996). Concise Chemical Thermodynamics. 2nd edition.

[24] Mpela, A. N. (2008). *A process synthesis approach to low-pressure methanol/dimethyl ether co-production from syngas over gold-based catalysts.* PhD Thesis, Republic of South Africa: University of the Witwatersrand, Johannesburg.

[25] Chen, W., Lin, B., Lee, H., & Huang M. (2012). One-step synthesis of dimethyl ether from the gas mixture containing CO_2 with high space velocity. *Applied Energy,* 98, 92-101.