An Automated Systematic Synthesis Framework for Determining the Most Viable Reaction Pathway Prior to Extensive Design Procedures: The Conversion of CO_2 to Value Added Products

Jaimee Jugmohan[1], Josias van der Merwe[2], Mulenga Bwalya[3]

[1, 2, 3]School of Chemical and Metallurgical Engineering, University of the Witwatersrand, 1 Jan Smuts Avenue, Johannesburg, 2000, South Africa

Email address: [1]jaimeejugmohan @ gmail.com, [2]Josias.VanDerMerwe @ wits.ac.za, [3]mulenga.bwalya @ wits.ac.za

Abstract— *Process feasibility is not limited to economic gains that the process is able to provide, but also encompasses the environmental impact associated therewith. Consequently, there are many research studies targeting the development of environmentally friendly reaction pathways. With the constant rise in novel chemical reaction pathways, the design of new chemical plants can prove to be challenging, with engineers focusing much of their design resources into finding the optimal reaction pathway to be utilized as the foundation for the chemical process. As such, the analysis of all reaction pathways associated with a single product can be a difficult and time-consuming task. This paper presents a novel automated tool that is able to systematically analyze a reaction pathway database, providing the user with a reduced search space containing only the theoretically viable reaction systems. The resulting search space not only eliminates the pathways that may be environmentally or economically infeasible, but also ranks the feasible pathways in order of their viability, based on the draw-offs covering the aforementioned feasibility criteria. The model presented within this paper focuses solely on the hydrogenation of carbon dioxide, in the production of methanol and dimethyl ether. This reactive system was chosen to highlight the effectiveness of the tool, whilst also aiming to utilize, and ultimately reduce, the high carbon dioxide levels within the atmosphere. Methanol and dimethyl ether have proven to be prominent in the energy industry, acting as an alternative energy source that can be used to meet the rising energy demands of a growing population. Throughout the course of the developed tool, all possible reaction pathway combinations leading from the reactant to the product are considered through a superstructure approach. The tool also incorporates basic designs of the respective reaction pathway combinations, as a means by which to determine the cost of the unit operations required to meet the operating conditions, as well as the necessary separation systems. This provides the user with a comprehensive view of the reaction systems, allowing for the most viable reactive system to be determined prior to any extensive design procedure, maximizing the efficiency of the design process.*

Keywords— *Automated Tool; Reactive system; Carbon dioxide; Methanol; Dimethyl Ether; Feasibility; Process Network Synthesis.*

I. INTRODUCTION

A significant portion of recent studies revolve around the advancement and optimization of existing processes, in an attempt to increase their economic and environmental feasibility. However, it is possible that a novel reaction pathway, or a combination thereof, could provide greater efficiencies, or lower operating costs, than what can be achieved through optimization of existing processes. The concern, however, lies in finding this specific pathway amongst the numerous documented reaction pathways to date. Such a task could prove to be time-consuming and an inefficient use of design resources.

This article presents a novel, automated systematic synthesis framework that aims to address the aforementioned concerns in a timeous manner, when utilized in conjunction with a reaction pathway database (RPD). This tool systematically analyses reaction pathways, eliminating those economically and environmentally infeasible options, allowing for design resources to be more focused on pathways with a greater chance of implementation.

II. LITERATURE REVIEW

Process Network Synthesis (PNS) is defined as the design and optimization of a chemical process, through the use of its associated mass and energy balances. [1] Often the reaction pathway within the process is considered to be the main area of focus. However, when analysing and assessing any reaction pathway, it is not feasible to account for all of the possible conditions that could occur within the process. Therefore, with each condition lies a simplifying assumption. Whilst this does tend to simplify the problem to an extent where it can be managed, each assumption lowers the accuracy of the solution in relation to the original problem.

In the year 1982, novel reaction pathways were analysed through the use of the Gibbs free energy concept. This development focused on the consideration of multiple reaction pathways simultaneously. However, since the approach taken involved two variable parameters, this resulted in an infinite number of pathways within the search space. [2] The number of reaction pathways was later contained through the introduction of thermodynamic feasibility into the screening process. [3] Other factors that were introduced into this analysis procedure included economics and safety factors. [4]

In the 2000s, a hierarchical procedure that made use of economic and thermodynamic feasibility was developed, with a consideration for kinetic desirability. Furthermore, the combinatorial approach used, allowed for a reaction that was previously deemed to be unfavourable, to be achieved through the combination of multiple favourable routes. [5] The

shortcoming of this research however is that the use of thermodynamic feasibility did not account for the conversion of the reaction. Furthermore, the economic considerations were considered on an input/output basis, and did not incorporate the equipment required to achieve the desired reaction conditions.

The integration of the P-graph framework extended to reaction pathway identification and synthesis in 1997. This concept provides a superstructure network that allows for all possible combinations to be considered. [6] In 2001, the P-graph was utilized for catalytic reactions [7], with this work also being verified later that same year. [8] The application of the P-graph was also used as a means for determining reaction pathway mechanisms in 2018, where the mechanism behind the catalytic partial oxidation of methanol was investigated. [9]

In 2018, Lakner et al. introduced the concept of startable reactions into the P-graph concept, stating that a reaction is considered to be startable if it is able to achieve steady state when only the reactants are available. This ensures that intermediary reactions are not considered and classified on their own within the P-Graph superstructure. [10] However, the shortcoming of this work was that the term 'feasibility' was simply an indication of whether a reaction pathway is considered possible, without taking into account conversions, production rates and current economics.

This was addressed by Jugmohan et al. in 2020, who looked at the development of a systematic synthesis framework to determine the optimum reaction pathway, using search space reduction. [11] The concern with this work is that the framework requires different software platforms, i.e. P-Graph, Studio ®, MATLAB, Aspen Plus ® and Microsoft Excel, with the data in each software being manually extracted and inputted into the next software. This requires access to all four software platforms. Furthermore, the framework is time consuming, and the manual transfer of data between these platforms increases the possibility of human error, thereby reducing the practicality and application of this framework industrially.

Additionally, the framework developed by Jugmohan et al. (2020) requires the manual design of each case study within Aspen Plus ®. As a result, it is possible that inconsistencies will develop between the case studies, therefore making comparisons between the processes ineffective. One of the major concerns with this work, was that each individual reaction within a reaction system was treated independently, assuming that reactions within a single reactor can be isolated. This however, is not the case, as it is common to have multiple reactions occurring within a reactor simultaneously, under specific reaction conditions, or in the presence of a specific catalyst. Therefore, all reactions must be considered as a unit when determining the number of possible reaction pathway combinations.

III. PROBLEM STATEMENT & MOTIVATION

The growing populations and increased energy demand that has been seen in recent years, has necessitated an increase in the use of fossil fuels as the primary energy source. Such excessive usage of fossil fuels does not promote sustainable development, and in turn lowers the global fossil fuel reserve considerably. In fact, studies have shown that with

approximately 70% of the energy demand being met though fossil fuel combustion, sources such as natural gas and coal are likely to be depleted by the years 2068 and 2169, respectively. [12]

As a result, the strain of fossil fuels must be lowered in meeting future energy demands, making it imperative to explore alternative and more environmentally friendly energy sources. This can be achieved through the utilization of greenhouse gas (GHG) emissions, such as carbon dioxide (CO_2). GHG emissions are gases that exist within the atmosphere, trapping heat and radiant energy, thereby resulting in climate changes and ozone depletion. [13]

CO_2 can be utilized through chemical reactions in the production of alternative fuel sources such as methanol and dimethyl ether (DME), to name a few. [14] As a result, the application of the tool developed within this article is demonstrated using a reaction pathway database focusing on the hydrogenation of CO_2 in the production of the aforementioned alternative fuels. This will not only highlight the efficacy of the tool, but will also draw attention to its use in exploring possible alternative energy sources.

Another concern that this tool aims to address is the use and allocation of design resources. There are many reactions that focus on the hydrogenation of CO_2, and to be able to better allocate design resources, the most viable pathways must be identified at an early stage. Often the heart of any chemical process is deemed as being the reactor unit operation. [15] As a result, the developed tool utilizes a database populated with reaction pathways, in order to find the most viable system. The strength of such a tool lies in the fact that it is based on a database, and as such the database can be adjusted or expanded accordingly, making this tool more generic in its application. Furthermore, the automated nature of this tool requires minimal interaction with the user, after the necessary input has been provided to the tool, making it easier and quicker to utilize.

IV. CODE SUMMARY

The code developed, and presented within this article, comprises of four main stages, as follows:

- The development of the reaction pathway database
- Determining the number of possible reaction pathway combinations
- Process design (mass and energy balances) and the costing of each case study
- Analysis of design and search space reduction using various criteria

The sections to follow details the explanation and requirements that surround each of the stages within this code.
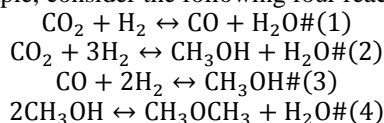
V. REACTIONS PATHWAY DATABASE (RPD) DEVELOPMENT

During this stage of the code, the user is prompted to enter the necessary reactions that are to be analysed. This database comprises of the reaction pathways, and their associated operating conditions, catalysts and conversions. The reference from which the pathway was extracted should also be noted as a means by which to cross-reference case studies in the reduced search space, i.e. the output of the automated tool developed.

During the construction of the RPD, it is not necessary to have the reaction kinetics. The reaction pathways will be analysed using the specified conversion noted in the RPD, aligning with the source from which the pathway was extracted. Once the final search space has been produced to the user at the end of the code, the user can then further analyse the pathway by means of reaction kinetics, focusing their design resources into one specific pathway.

VI. Reaction Pathway Combinations

It is possible that pathways previously deemed to be unfavourable, can be combined with one another in an attempt to increase their feasibility. In these cases, the product of one reaction, can be the reactant to the second reaction, thereby serving as an intermediary in the overall process. In this way, novel reaction pathway combinations from various sources are also considered. With the code developed, a total of 4 sub-reactions can exist or be combined within any of the reactive systems. In other words, the individual reactions are treated as a superstructure, with the analysed reactive systems being subsets of this superstructure.

For example, consider the following four reactions:
$$CO_2 + H_2 \leftrightarrow CO + H_2O \#(1)$$
$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \#(2)$$
$$CO + 2H_2 \leftrightarrow CH_3OH \#(3)$$
$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \#(4)$$

Assuming that each of these reactions are independent of one another, there are two reactions that can proceed with a CO_2/H_2 feed stream, namely (1) and (2). However, by combining the aforementioned reactions, the number of possible reactive systems with the same feed stream extends to 5 reactive systems. An example of one such reactive system is the combination of (1), (3) and (4). In this way the products of the previous reactions become intermediates within the reactive system. Furthermore, this allows for alternative products to be produced from the aforementioned feed stream.

This ensures that all possible reactive systems are considered from the RPD.

VII. Process Design

A. Generic Process Design

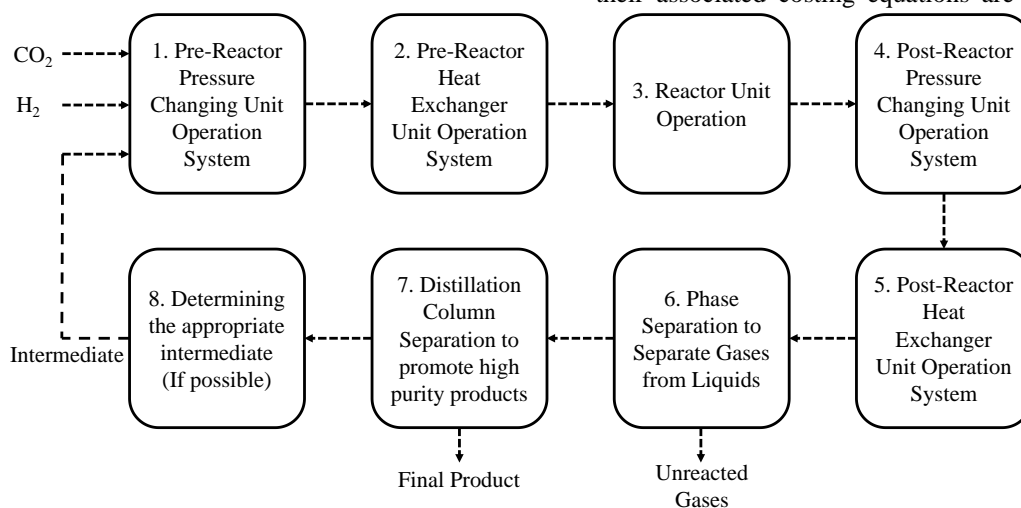Each reaction pathway combination was designed using a generic flowsheet that was applied for each sub-reaction in the reaction pathway system. This allowed for consistency throughout the designs, thereby promoting effective and accurate process comparisons.

The generic structure used per sub-reaction, within a reaction system, is shown in Fig. 1.

As seen in Fig. 1, there are 8 main stages in the design of any of the generic case studies. The first two stages focus on achieving the reaction conditions, as per the RPD previously developed. Stages 4 and 5 focus on achieving the conditions that are necessary for the separation system required.

B. Design Assumptions

As with any simulation or design procedures, there does exist a certain degree of uncertainty, brought about by the lack of information that is available within these early design stages. As a result, the following assumptions were made during the design stages:

- All pressure-changing unit operations are considered to be isothermal, i.e. the temperature does not change across these unit operations
- All heat exchanger unit operations are considered to be isobaric, i.e. the pressure does not change across these unit operations. This is achieved by varying the diameter of the pipe entering and leaving the heat exchanger, to ensure that the exit stream maintains the pressure of the inlet stream.
- The recovery of the phase separators is set at a 95% recovery of the unreacted gases.
- All operating temperatures and pressures within the plant design are above atmospheric conditions, ensuring that there is no need for cryogenic or vacuum systems, respectively. As a result, all hydrogen and carbon monoxide are expected to remain in the gas phase in its entirety, as these conditions are considerably higher than the critical temperatures and pressures of these chemical species.
- The product stream must have at least a 99% mass purity in order to promote the sale within the current market.
- Unit operations that are smaller than the lower limits of their associated costing equations are costed using the

Fig. 1: Generic Flowsheet design for each sub-reactive with the reactive system/case study

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lower costing limit, accounting for a worse-case costing scenario.

C. Equation of State (EOS)

An EOS model highlights the relationship that exists between the pressure, volume and temperature of the components within a stream. The EOS is able to provide a thermodynamic description on the state of matter that the substance is expected to be in, when exposed to specific conditions. [16]

The selection of the correct EOS is imperative, as it is the thermodynamic model that determines changes in the physical properties of the stream, as well as the enthalpy and the equilibrium. If an inaccurate or incorrect model is chosen, this is likely to cause convergence problems and inaccurate results.

During the design of each process, the Peng-Robinson EOS is utilized. This EOS is commonly used in the petroleum industry, also encompassing the products of methanol and DME. Furthermore, the Peng-Robinson EOS is able to handle liquid and vapor properties. [16] This makes its use ideal in the system demonstrated in this article, as this system contains both vapor and liquid process streams.

Equations (5) to (10) detail the necessary equations that are associated with the Peng-Robinson EOS, including the relationships that exist between pressure (P), temperature (T) and the molar volume (V_m). The Peng-Robinson factors (α. a, b and κ) are calculated using the critical temperature (T_c), critical pressure (P_c), ideal gas constant (R), reduced temperature (T_r) and the acentric factor (ω).

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m^2 + 2bV_m - b^2} \#(5)$$

Where:

$$a = 0.45723553 \frac{R^2 T_c^2}{P_c} \#(6)$$

$$b = 0.07779607 \frac{RT_c}{P_c} \#(7)$$

$$\alpha = \left(1 + \kappa\left(1 - \sqrt{T_r}\right)\right)^2 \#(8)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \#(9)$$

$$T_r = \frac{T}{T_c} \#(10)$$

Table I highlights the critical properties of the chemical species that are considered within this system, as well as their associated acentric factors.

TABLE I. Critical properties and acentric factor of chemical species within this system [17]

Specie	T_c (Kelvin)	P_c (bar)	Acentric Factor (ω)
CO_2	304.1	73.8	0.239
H_2	33.0	12.9	-0.216
CO	132.9	35.0	0.066
H_2O	647.3	221.2	0.344
CH_3OH	512.6	80.9	0.556
CH_3OCH_3	400	52.4	0.200

D. Sizing & Costing of Unit Operations

The sizing of the heat exchanger unit operations, were completed using the general heat transfer equation, as shown in (11).

$$Q = UA\Delta T_{LM} \#(11)$$

Equation (11) shows that the heat transferred across the streams within the heat exchanger (Q), is dependent on the area of the heat exchanger (A), the overall heat transfer co-efficient (U), and the log-mean temperature (T_{LM}).

The overall heat transfer co-efficient is dependent on the fluid present within the stream, as well as the utility that is used to promote the heat transfer. Table II details the ranges utilized for the overall heat transfer co-efficient.

TABLE II. Overall Heat transfer Co-Efficients utilized for the heat exchanger design [18]

Fluids	U (W/m².K)
Water to Water	1300 – 2500
Gas to Water	10 – 250
Light Organics to Water	370 – 750
Medium Organics to Water	240 – 650
Heavy Organics to Water	25 – 400
Water to Steam	2200 – 3500
Gas to Steam	25 – 240
Light Organics to Steam	490 – 1000
Medium Organics to Steam	250 – 500
Heavy Organics to Steam	30 – 300

The sizing of the pressure changing unit operations, in terms of its energy rating, were calculated through the use of the first law of thermodynamics, as demonstrated in (12). [19] The work (W) of the pressure-changing unit operation is calculated using its change in the pressure and volume (V).

$$\delta W = \int -PdV \#(12)$$

The assumption made previously, regarding pressure-changing unit operations, was that all of these units are isothermal in nature, indicating no temperature change. As a result, the only work that occurs in this instance would be that caused by the change in the pressure and volume of the components (PV work).

The diameter of the flash drums/phase separators (D_v) was calculated using (13), which utilizes the cross-sectional area (A_c) of the process vessel. The height to diameter ratio was set as 4. [20]

$$D_v = \sqrt{\frac{4A_c}{\pi}} \#(13)$$

The number of stages within the distillation column (N_{min}) followed the Fenske equation, represented by (14). [20] This equation utilizes the molar compositions of components A and B in the distillate and bottom stream (x_A and x_B), as well as their relative volatilities (α_{AB}).

$$N_{min} = \frac{\ln\left(\frac{\left(\frac{x_A}{x_B}\right)_{Dist}}{\left(\frac{x_A}{x_B}\right)_{Bottom}}\right)}{\ln(\alpha_{AB})} \#(14)$$

All unit operations within this automated tool are costed as per the costing procedure detail by Turton et al. (2009). [21]

E. The separation of CO2/DME

During the development of this automated tool, the separation of CO_2 from DME proved to be quite difficult, with

much of the DME product being lost in the purge stream. As a result, this caused a reduction in the production rate, and consequently, a reduction in the profitability of the process as well.

In order to address this issue, calcium oxide was used as a means for CO_2 capture in the stream. In this way, the carbon dioxide is reacted with calcium oxide, in order to form calcium carbonate, as shown in (15).

$$CaO + CO_2 \leftrightarrow CaCO_3 \#(15)$$
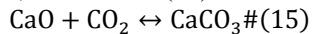
Not only has this proven to achieve effective removal of CO_2, with carbon capture rates as high as 90% being recorded [22], but the calcium carbonate product being formed, can be sold off as an additional process product. As a result, the profitability of the process is increased.

For the carbonation of CaO to be achieved, CO_2 must be reacted with CaO at $650^{\circ}C$ and at a CO_2 partial pressure of approximately 0.15 bar. [23] Therefore, in order to promote this reaction, and achieve the necessary partial pressure of CO_2, the carbonation process occurs before the separation of water, lowering the partial pressure of CO_2 in the stream.

VIII. Search Space Reduction Criteria

After the complete design of the processes associated with each case study, the case studies are compared with one another in order to eliminate those that are deemed to be infeasible, either from an economic or an environmental standpoint. There are a total of three search space reduction criteria that are utilized, with a final, fourth criterion being used to rank the remaining search space in order of their feasibility. This section details these criteria.

A. Criteria #1 – Economic Feasibility

The first criterion looks at the case studies from an economic standpoint, considering the input/output structure of the case studies. Here the profit of each case study is calculated, taking into account the cost of the reactants (C_R) required, as well as the sales potential of product (SP_P) that is produced with the possibility of being sold. There is a certain portion of the product that is lost within the separation process of each case study, therefore this criterion ensures that the efficiency of the separation system is also considered.

$$Profit = SP_P - C_R \#(16)$$

Equation (16) shows the annual profit potential that is possible from the case study in question, before accounting for other operational costs that may be incurred, such as labor and plant maintenance. In this way, any case study that yields a negative profit value, i.e. a loss, is excluded from the search space. The resulting search space then contains only those reactive systems that are considered to be financially feasible.

B. Criteria #2 – Environmental Benefit

The second criterion considers the environmental impact of these case studies. As mentioned previously, the amount of CO_2 in the atmosphere has increased drastically over the recent years, leading to many environmental concerns such as climate change. As a result, this criterion pays equal attention to the environmental gains possible from a specific case study.

There are many green sources that can be explored to meet the energy requirements associated with each unit operation required within a case study. However, the concern that is commonly experienced with green energy is their intermittent and fluctuating nature. Furthermore, the energy efficiency of these sources, such as solar and wind energy, are considered to be low in comparison to the traditional fossil fuel energy potential. As a result, natural gas is used as the primary energy provider for each case study. By meeting the energy requirements of the plant in this way, there is no additional strain that is placed on the current electricity grid.

Assuming that the natural gas is composed primarily of methane gas, the combustion of natural gas occurs by means of the following chemical equation:

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O \#(17)$$
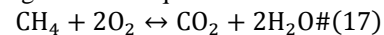
As seen by (17), this combustion process involves the production of CO_2. As mentioned previously, the code developed was specifically applied to a CO_2/H_2 system in an effort to reduce the atmospheric CO_2 levels. Therefore, in order for a case study to still be considered environmentally viable the net atmospheric CO_2 reduction (ATM_{CO2}) must be considered, taking into account the unreacted CO_2 (UNR_{CO2}), the CO_2 produced during the combustion of methane ($COMBUST_{CO2}$) and the CO_2 taken in by the process (IN_{CO2}). This was accomplished through the use of (18).

$$ATM_{CO2} = UNR_{CO2} + COMBUST_{CO2} - IN_{CO2} \#(18)$$

Based on (18), in order for a case study to be considered environmentally beneficial, the net atmospheric CO_2 should be negative, implying that the process is taking in more CO_2 than it is emitting. Furthermore, the CO_2 that is produced through the combustion of natural gas, can later be recycled to the feed of the reactive system, lowering the cost of the reactants involved, and increasing the associated profit of the case study. This would be possible under steady state conditions.

Therefore, any case study that exhibits a positive net atmospheric CO_2 value, shows that CO_2 is being released into the environment, and is excluded from the search space as being environmentally infeasible. Furthermore, as natural gas is required constantly to keep the plant operational, this can be accounted for within the annual profit of the case study, as was previously calculated by (16). The revised profit calculation (Adj Profit) can now be represented by (19), accounting for the annual cost of natural gas (C_{NG}).

$$Adj\ Profit = SP_P - C_R - C_{NG} \#(19)$$

C. Criteria #3 – Payback Period

The final search space reduction criterion considers a simplified version of the payback period of the plant. In order for a plant to be implemented, there must be capital that is invested into the process. This capital is often obtained from potential investors, however, for the proposed plant to be considered by an investor, it must highlight the economic benefit that they would gain from their investment. This is often seen by the return that is received on their initial investment (ROI). One of the main factors considered by any potential investor, is the time period required to see this ROI.

Often a medium to large production plant is expected to be paid off in the region of 2 to 10 years. [24] Therefore, for the third search space reduction criterion, the payback period associated with the unit operations is considered. This considers the time period that is required for all unit operations within the process to be paid off, using the adjusted annual profit, as revised in (19). This payback period (PBP) was calculated using (20), accounting for the cost of the pressure-changing unit operations (C_P), heat exchangers (C_{HE}) and the separation systems (C_S).

$$PBP = \frac{C_P + C_{HE} + C_S}{Adj\ Profit} \#(20)$$

D. Ranking the final search space – Performance Index

The application of the aforementioned three search space reduction criteria results in a final search space where all case studies exhibit both economic and environmental feasibility. At this stage, it is necessary for the user of this tool to know which case study is considered to be the most feasible, and should be investigated first. Therefore, a performance index (PI) is required to rank the remaining case studies. This performance index must find the case study that has the best compromise between economic and environmental benefits. Often economic gains decrease, with increasing environmental benefits, as a greater capital investment is required. Therefore, a ratio of these factors was used to express the draw off between economic and environmental gain, as shown in (21), where OC_{Annual} represents the annual operating costs associated with the process.

$$PI = \frac{ATM_{CO2}}{OC_{Annual}} \#(21)$$

Equation (21) provides the user with a performance index, where a higher value is indicative of a higher environmental benefit and a lower operating cost.

IX. APPLICATION

The tool developed throughout the course of this article was applied to a basic RPD, containing pathways that focus on the production of methanol and DME through the hydrogenation of CO_2. Table III highlights the basic RPD used in demonstrating the application and usefulness of this tool. In Table III, the temperature (T) is given in degrees Celsius (^oC), the pressure (P) is given in bar, and the conversion is given as a percentage (%) of the first reactant.

TABLE III. Basic RPD to demonstrate the application of the tool developed

No	Reaction	T	P	X	Ref
1	$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$	240	80	96	[25]
2	$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$	400	25	87.2	[26]
3	$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$	400	20	10	[27]
4	$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$	280	20	20.7	[28]
5	$CO_2 + H_2 \leftrightarrow CO + H_2O$	360	1	58.2	[29]
6	$CO + 2H_2 \leftrightarrow CH_3OH$	290	14.5	1.35	[30]

Table IV highlights the inputs that are required from the user in the operation of the developed tool.

Based on the RPD presented in Table III, a CO_2/H_2 feed stream can be utilized in 4 of the six reactions presented, with the main product being either syngas or methanol.

TABLE IV. Input data required from the user

Factor Input	Value	Units	Ref
CO_2 Feed basis	100	kmol/hr	n/a
Excess H_2 Feed	50	%	n/a
Pressure-changing Efficiency	74	%	[31]
CEPCI (2018)	603.1	dimensionless	[32]
Pressure of HE Utility	3	bar	n/a
Steam Temp Change	50	Kelvin	n/a
Cooling Water Temp Change	20	Kelvin	n/a
Cost of CO_2	0.1	$/kg	[33]
Cost of H_2	1	$/kg	[34]
Cost of CaO	0.12	$/kg	[35]
Cost of NG Utility	0.48	$/kg	[36]
Sales Potential of MeOH	0.47	$/kg	[37]
Sales Potential of DME	0.99	$/kg	[38]
Sales Potential of $CaCO_3$	0.26	$/kg	*
Distillation Recovery	99.99	%	n/a

* Based on the average current market price

Through the application of the aforementioned code developed, there are a total of 9 case studies/reaction pathway combinations derived from the RPD, utilizing the same CO_2/H_2 feed stream, extending the possible products to encompass DME. Table V details the case studies/reaction pathway combinations achieved, and deemed possible, through this tool.

TABLE V. Case Studies derived from the Basic RPD

CS	Reaction	T	P	X	Ref
1	$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$	240	80	96	[25]
2	$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$	400	20	10	[27]
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Through the automated code developed in this manuscript, the 9 case studies shown in Table V can be reduced to a single case study, i.e. Case Study 5, which is the only reactive system that exhibits economic and environmental feasibility. Table VI highlights the results obtained from this automated tool relating to Case Study 5.

The resulting reaction pathway system, i.e. Case Study 5, aligns with the final results found by Jugmohan et al. (2020), attesting to the efficacy and reliability of the tool developed.

The total time required to run the tool was 1024.50 seconds, approximating to roughly 17.07 minutes. This tool was developed and run on a Dell Intel® Core™ i5-2520M CPU @ 2.50 GHz with 8.00 GB Installed Ram (7.88 GB usable).

TABLE VI. Properties of Case Study 5

Case Study Number	Value	Units
CO_2 Feed	34 855.92	tons/annum
Methanol Produced	3 113.91	tons/annum
Methanol Purity	99.93	mass %
Dimethyl Ether Produced	15 251.25	tons/annum
Dimethyl Ether Purity	99.36	mass %
Calcium Oxide Needed	1 115.72	tons/annum
Calcium Carbonate Produced	1 991.34	tons/annum
Total Reactant Cost	10 804 502.58	$/annum
Total Product revenue	17 080 027.62	$/annum
Cost of Heat Exchanger System	1 264 117.63	$
Cost of Pressure-Changing System	4 247 435.68	$
Cost of Separation System	1 271 266.16	$
Annual Profit	6 275 525.03	$/annum
New CO_2 Environmental Impact	-2 9530.44	tons/annum
Payback Period	1.25	years

X. CONCLUSION

The automated tool developed, and explained, within this manuscript, was able to systematically construct reaction pathway combinations, before analyzing each combination thereof. Accounting for both the economic and environmental benefits provided by each reactive system, the tool is able to detect and provide the user with the most viable option, to be investigated further. As a result, multiple reaction pathways are able to be considered in a short amount of time, with the final search space only including those reactions with the possibility for implementation. This allows for design resources to be more effectively allocated during the initial design stages. The alignment of this novel tool with the results of work previously conducted in this area, attests to its efficacy, proving that this tool can be a great asset to the chemical industry, and play an integral role in the future of process synthesis and optimization.

XI. NOMENCLATURE

Table VII details the symbols used throughout the course of this manuscript and their associated descriptions and units.

TABLE VII. Symbols utilized in this manuscript and their associated descriptions

Symbol	Description	Units
P	Pressure	bar
R	Ideal Gas Constant	(L.bar)/(mol.K)
T	Temperature	Kelvin
V_m	Molar Volume	L/mol
α, a, b, κ	Peng-Robinson Parameters	n/a
T_c	Critical Temperature	Kelvin
P_c	Critical Pressure	bar
ω	Acentric Factor	n/a
T_r	Reduced Temperature	n/a
Q	Heat Energy	kW
U	Overall Heat Transfer Co-Efficient	W/m².K
A	Heat Exchanger Area	m²
ΔT_{LM}	Log Mean Temperature	Kelvin
W	Work	kW
D_v	Vessel Diameter	m
A_c	Cross-Sectional Area	m²
N_{min}	Minimum Number of Trays	n/a
x_A, x_B	Molar Fraction of Specie A and B	n/a
α_{AB}	Relative Volatility	n/a
Profit	Annual Profit	$/annum

Symbol	Description	Units
SP_P	Sales Potential of Products	$/annum
C_R	Cost of Reactants	$/annum
ATM_{CO2}	Net Atmospheric CO_2 impact	tons/annum
UNR_{CO2}	Unreacted CO_2 flow rate	tons/annum
$COMBUST_{CO2}$	CO_2 produced from NG combustion	tons/annum
IN_{CO2}	CO_2 into the process	tons/annum
Adj Profit	Adjusted annual profit	$/annum
C_{NG}	Cost of Natural Gas Utility	$/annum
PBP	Payback Period	years
C_P	Cost of Pressure-Changing Units	$
C_{HE}	Cost of Heat Exchangers	$
C_S	Cost of Separation Systems	$
PI	Performance Index	dimensionless
OC_{Annual}	Annual Operating Costs	$/annum

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