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Reactive distillation for methanol synthesis: Simulation-based design methodology

Shashwata Ghosh and Seethamraju Srinivas†

Department of Energy Science and Engineering, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India
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Abstract−A simulation-based design methodology for configuring a reactive distillation (RD) column for methanol synthesis is presented in this work. Unlike other processes using RD, all the reactants involved in methanol synthesis are gaseous and, therefore, the conventional methods used for the design of RD columns cannot be used. The simulation-based design algorithm also gives better insights into the process. RD for methanol synthesis requires an inert solvent and the column configuration has side coolers on the stages to remove the heat of reaction. The developed algorithm aims to maximize the methanol production, while minimizing the solvent requirement and the number of side coolers. The methodology has been demonstrated for three different feed syngas compositions. It is observed that the performance of RD is either at par with, or superior to, the conventional process for the studied cases. A multi-parametric sensitivity analysis shows that the solution obtained using this design algorithm is within 0.3% of the local optimum. The effect of solvent flowrate on the column sizing and economics and the possibility of multiple steady-states is also illustrated.

Keywords: Reactive Distillation, Methanol Synthesis, Solvent, Optimization, Simulation, Design

INTRODUCTION

Methanol is a very important petrochemical intermediate that is used in the manufacture of many chemicals such as formaldehyde, acetic acid, methyl *tert*-butyl ether (MTBE). The methanol economy, advocated by Olah et al. [1], considers methanol as a medium of energy storage, transportation fuel and source of synthetic hydrocarbons. New uses of methanol, such as direct gasoline blending, olefin synthesis and use of DME as a fuel, have led to an increased demand for methanol in China, which rose from 12% of the global methanol demand in 2000 to 54% in 2015 [2]. The global methanol production has almost doubled in the last ten years and is projected to grow and increase to nearly five times the present capacity of 98 MMT by 2050 [3]. Currently, large scale methanol plants of capacities up to 10,000 MT/day [4] are being considered in view of the rising demand. The conventional method of methanol production from syngas uses a gas-solid packed bed reactor (PBR) in which the reactants and products constitute the gas (vapor) phase and the catalyst is the solid phase. It involves the following reactions:

$$CO+2H_2 \leftrightarrows CH_3OH \qquad \Delta H^0_{298\,K}=-91\ \text{kJ/mol} \qquad (1)$$

$$CO_2+3H_2 \leftrightarrows CH_3OH+H_2O \qquad \Delta H^0_{298\,K}=-50\ \text{kJ/mol} \qquad (2)$$

$$CO_2+H_2 \leftrightarrows CO+H_2O \qquad \Delta H^0_{298\,K}=+41\ \text{kJ/mol} \qquad (3)$$

Reactions (1) and (2) are highly exothermic and necessitate cooling requirements in the reactor to remove chemical equilibrium limitations and prevent deactivation of the solid catalyst. Reaction (3), also known as the reverse water gas shift reaction, is a mildly endothermic side reaction. Conventional reactors are cooled either by introducing cold syngas shots in between the adiabatic packed beds (ICI type) or by boiling water on the shell side of the reactor with catalyst packing in the tubes (Lurgi reactor). Another process, referred to as the liquid phase process, uses an inert solvent as the reaction medium to absorb the heat of reaction. In this process, methanol formation takes place on solid catalyst present in the solvent and higher reactant conversions are observed due to the lower reactor temperatures resulting from direct heat transfer to the liquid solvent. Some process intensification techniques aim at removing the products (methanol and water) in-situ to overcome chemical equilibrium limitations; these include the use of membrane reactors [5] or adsorbents [6] (sorption enhanced methanol synthesis). Reactive distillation (RD) is another process intensification technique applied to methanol synthesis and is based on liquid phase methanol synthesis. RD has already been successfully demonstrated for production of methyl acetate and methyl *tert*-butyl ether [7] and design of RD processes for new applications is also being studied, e.g., formic acid production with dividing wall columns [8], lactic acid recovery [9], using heat integration methods. Application of RD for methanol synthesis was first reported in a patent by Nemphos et al. [10], who demonstrated methanol production in a once-through reactive column with catalytic packing using n-octane as an inert solvent. Further studies on modeling and simulation for analyzing the feasibility of reactive distillation for methanol synthesis were reported in our previous works [11-13] and it was shown that per pass CO conversion of ~78% is achievable for an optimized RD column, operated in a once-through mode. It was also shown that the performance by RD is comparable to the conventional process in terms of the reactant conversions and methanol production [14]. In the current work, a simulation-based methodology was developed to design an RD column for methanol synthesis. The methodology was demonstrated through a few case-studies

†To whom correspondence should be addressed.
E-mail: s.srinivas@iitb.ac.in

using different syngas compositions and the performance of the finally designed RD columns was compared with the conventional process scheme.

Various methods for the conceptual design of RD columns are available in literature. An extensive review of these methods is presented by Almeida-Rivera et al. [15], who broadly classify these into (a) graphical, (b) optimization-based and (c) heuristic based. The former is based on the graphical analysis of the composition diagram and includes techniques like the fixed-point method, based on the boundary value design method for non-reactive columns, which requires product compositions as specifications. Initial studies on fixed-point methods for the design of RD columns used assumptions of constant liquid hold-up on reactive stages, negligible heat of reaction, constant molar heat of vaporization, vapor-liquid equilibrium on each stage [16,17]; however, Okazinski et al. [18] later relaxed these assumptions and presented a much more generalized approach. The fixed-point approach is applicable to both equilibrium and kinetically controlled reactions. A recent modification of the fixed-point method was published in 2016 [19] that considers the effect of temperature on reaction and separation for RD using a quaternary system. Another method, referred to as the Statics analysis technique, is based on topological and thermodynamic analysis of distillation diagrams [20]. Other graphical methods are the attainable region technique [21] for RD which is mainly used to obtain sequences of reactors in process synthesis, extensions of conventional graphical techniques like the McCabe-Thiele and Ponchon-Savarit methods [22]. However, a major disadvantage of these graphical methods is their intrinsic graphical nature. Though graphical methods can be applied to systems with more than three chemical species, it is difficult to apply them for methanol synthesis because of the presence of a number of non-condensable species, which increase the complexity of the system. Moreover, these methods are not designed for systems in which all the reacting species are gaseous, as in case of methanol synthesis.

Optimization-based methods to find the optimal design of RD columns are based on mathematical programming. Ciric and Gu [23] used mixed integer non-linear programming (MINLP) to minimize the total annual cost for ethylene glycol synthesis by RD. MINLP optimization for the design of two industrial RD processes, MTBE synthesis and methyl acetate synthesis, was also demonstrated by Stichlmair and Frey [24]. Graphical methods are most useful for evaluating the feasibility of RD systems, whereas the optimization techniques are capable of generating detailed designs [15]. However, as pointed out by Malone and Doherty [25], mathematical optimization must be exercised carefully as it is highly dependent on the feasibility constraints and sensitivities of the model, which may lead to convergence issues. They also do not provide much insight into the process vis-à-vis the graphical methods. Since methanol synthesis involves complex vapor liquid equilibrium (VLE) calculations, which often lead to convergence issues, mathematical optimization is not resorted to in the present work. Also, it is important to have some insight into the process because of the model sensitivity and feasibility issues, which is not offered by optimization-based design methods. Srinivas et al. [26] developed a simulation-based design algorithm to design an RD column for Fischer-Tropsch synthesis (FTS). Methanol synthesis is similar to FTS as both these processes involve gaseous reactants (CO and H_2 mainly) and the reaction takes place in a solvent. However, the same design algorithm is not applicable in this case, since FTS involves multiple products and the design algorithm involves engineering of product selectivity in FTS, which is not the case with methanol synthesis. Therefore, a new simulation-based design algorithm is developed for this system, which is the novelty of this work. It may be noted that RD processes involving gaseous reactants alone (CO and H_2 in this case) and low boiling point products (CH_3OH in this case) are particularly difficult to design. The presence of non-condensable species along with condensable components is responsible for increasing the complexity of this design problem. The current work proposes a sequential design strategy to address this problem.

SIMULATION MODULES AND PROCESS DESCRIPTION

The process simulation is performed in Aspen Plus® v8.4 [27] because of its strong thermodynamics database and robust numerical solvers. A schematic of the simulated process is shown in Fig. 1. Fresh syngas compressed to a pressure of 52 bars in a multi-stage compressor (CMP-1) is fed to the bottom of a RD column (RDC), after being heated to the desired temperature in a heater (HT-1). Two more feed streams enter the RDC - a gas recycle stream composed of the unreacted syngas and a solvent feed, comprising recycled and fresh (make-up) solvent, i.e., squalane. The gas recycle stream is fed to an intermediate stage in the RDC, whereas the solvent is fed to the top of the column. Prior to their entry in the reactor, the temperatures of the recycled gas and solvent streams are adjusted in a heater (HT-2) and a cooler (CL-1), respectively. The heaters and coolers (HT-1, HT-2 and CL-1) are used to adjust the temperatures of the feed streams when using the proposed design algorithm. The RDC is simulated with the assumption of "equilibrium stage" using the "RadFrac" module, which performs rigorous distillation column calculations based on solution of the MESH equations [28]. The RDC does not have a reboiler since syngas is fed to the bottom and serves the purpose of a reboiler which supplies vapor to a distillation column. The RDC is also devoid of a reflux since it was observed that recycling of the unreacted gases to the column renders the reflux redundant, as pointed out in our previous work [14]. A pressure drop of 2 bars is used in the RDC. Two streams, a vapor and a bottom product stream, exit the RDC. The bottom stream is rich in the solvent and is recycled, whereas the vapor product stream consists of the produced methanol, water and unreacted gases. The vapor product stream is cooled in a condenser (C-1) to condense the produced methanol and water in a separator vessel (F-1), which leave the unit in the crude methanol stream. The unreacted gases from F-1 are compressed in a recycle gas compressor (CMP-2) and fed to the RDC after purging off a small amount (2 mol%) of the gases.

In practice, the crude methanol stream is further purified to obtain commercial grade methanol by distillation. However, this work deals with the design of the RD column configuration and, hence, the downstream processing step is not shown. A similar process flow diagram was also used in our previous work [13] to evaluate

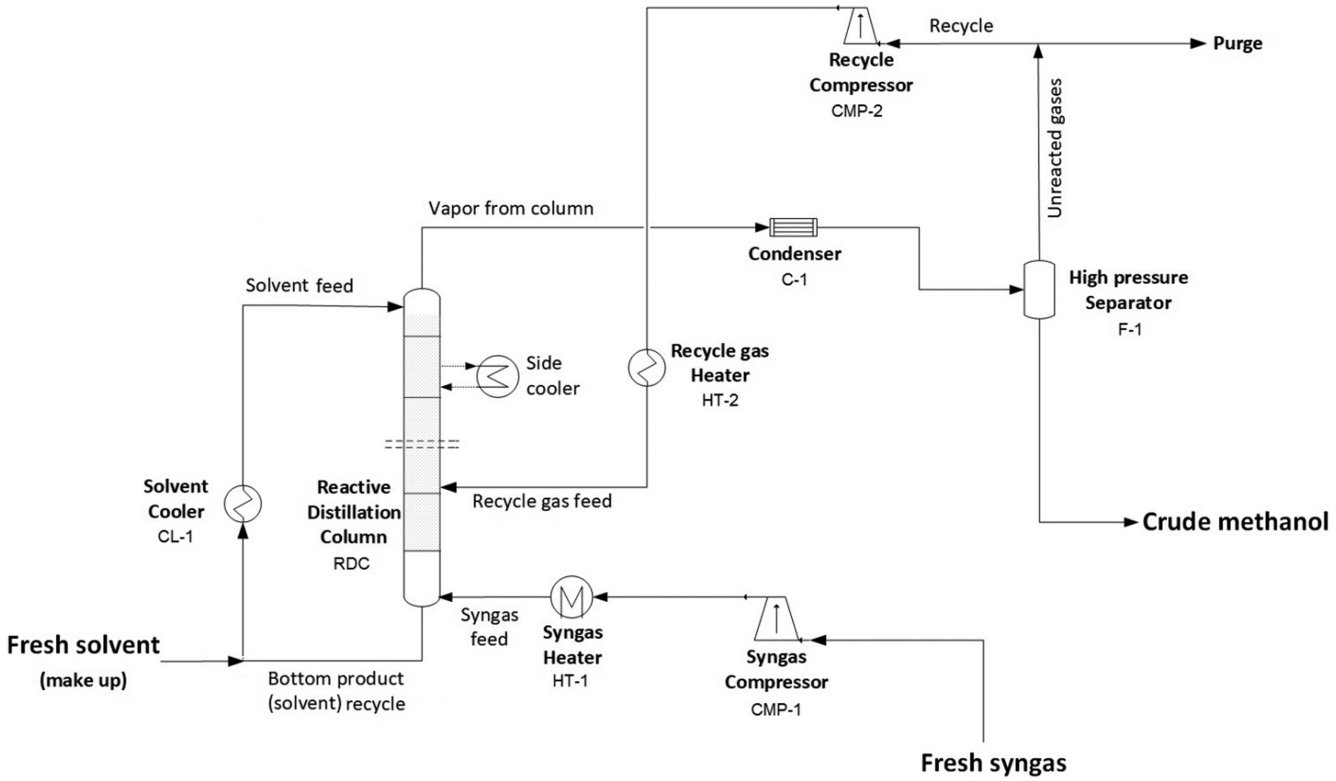

Fig. 1. Schematic of the simulated process for methanol synthesis by RD.

the performance of an RD column with recycle included.

The power law type kinetic models of van der Laan et al. [29] and Kobl et al. [30] are used in the RDC for modeling methanol synthesis. The kinetic expression used in this work for liquid phase methanol synthesis was developed for the conventional Cu-ZnO-Al_2O_3 catalyst (Haldor Topsoe MK101) with squalane as the solvent and, therefore, the simulation results presented are for the same catalyst. The catalyst developed for the vapor phase process offers lower methanol production rates when used for liquid phase methanol synthesis. Krishnan et al. [31] report that rates of methanol production in the liquid phase process are lower by 2-3 times than the vapor phase process. The VLE characteristics of the system are modeled with the Soave-Redlich-Kwong equation of state with binary interaction parameters reported by Graaf et al. [32]. Details of the thermodynamic and kinetic models are given in our previous work [11].

The subtle interplay of kinetics and phase equilibrium is very crucial in RD processes, and decides the performance of the process. This interdependence has been described in our previous works on feasibility and parametric studies of RD for methanol synthesis [11-13].

DESIGN METHODOLOGY

1. Design Objectives

A number of parameters - temperatures of the fresh syngas, solvent and gas recycle streams, gas recycle feed stage, solvent flow rate, and number, location and duties of side coolers - need to be optimized to obtain an optimal RD column design for methanol synthesis. The design methodology described in this work was developed for a high-boiling non-polar solvent (squalane, $C_{30}H_{62}$) since it offers better performance in terms of syngas conversion and separation than a polar solvent (tetraglyme, $C_{10}H_{22}O_5$), as shown in our previous work [11]. Optimization of an RD column for methanol synthesis operated once-through necessitated the presence of side coolers on almost all the stages, which is practically not feasible. Also, reducing the number of side coolers lowers the capital costs. Hence, one of the objectives of the design methodology is to minimize the number of side coolers. The optimum RD column configuration also gave a better separation of methanol and solvent than a fully reactive column due to the presence of a few non-reactive stages. However, it is observed that non-reactive stages are not necessary when the unreacted gases are recycled to the RD column, and separation of methanol and solvent in a fully reactive column is comparable with the optimized once-through configuration. The presence of a large amount of non-condensable gases and the high boiling non-polar solvent aids separation and eliminates the need for non-reactive stages. It may also be noted that non-reactive stages increase the average temperature of the stages [11] and can pose difficulty in heat removal. Therefore, a fully reactive column configuration has been used in this work. Also, the solid catalyst has been distributed equally on all the stages of the column with a maximum permissible catalyst loading of 1,000 kg per stage. Another objective is to keep the solvent flow rate as low as possible. While a high solvent flow rate increases the costs, a low value of the same elevates the stage temperatures beyond per-

Table 1. The design problem

Objectives	Maximize methanol production Minimize solvent flow rate & number of side coolers
Decision variables	Feed temperatures (Syngas, Solvent, Recycle) Recycle feed stage Number & duty of side coolers Solvent flow rate
Constraint	Stage temperature$\leq\theta$ (a maximum permissible limit)

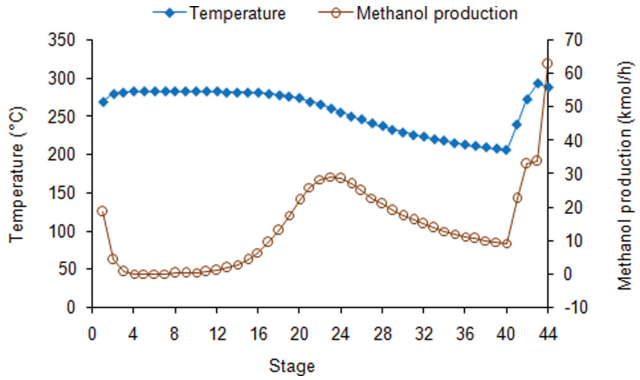

Fig. 2. RD column profiles before optimization using proposed design methodology.

missible limits. So, an optimum solvent flow rate is also desired. The main objective of the design methodology is to maximize the methanol production, while minimizing the solvent flow rate and the number of side coolers simultaneously. The objectives, decision (design) variables and constraint are listed in Table 1. The in-built Wegstein solver of Aspen Plus was used for the simulations involved in each of the steps of the design methodology.

2. Design Principle

Fig. 2 shows the profiles for temperatures and rates of methanol production on the individual stages in the RD column for one of the cases studied in this work prior to optimization by means of the developed design methodology. In the absence of chemical equilibrium limitations, the rate of methanol synthesis profile is expected to follow the temperature profile in the column. However, the rate of methanol synthesis profile shows a different trend due to the presence of chemical equilibrium limitations on stages 1-22. The design algorithm presented in this work aims to remove chemical equilibrium limitations by adjusting the temperatures of the feed streams and adding side coolers at suitable locations (stages) in the column to remove the heat of reaction so that both the temperature and reaction profiles are aligned to the extent possible. Since a number of process variables are to be optimized, the design algorithm aims to give an appropriate sequence of adjusting the variables to achieve the given objectives.

3. Design Algorithm

A schematic of the proposed algorithm for the conceptual design of a RD column for methanol synthesis is given in Fig. 3 and its steps are as follows:

Step 1: Start with a process schematic as shown in Fig. 1. Do not put any non-reactive stage and side coolers in the RD column. Fix the gas hourly space velocity and calculate the total amount of catalyst to be loaded in the RD column. Calculate the number of theoretical stages according to the total amount of catalyst that can be accommodated per stage. Fix the stage receiving the gas recycle and temperatures of the three feed streams - solvent, fresh syngas and recycle gas. Fix the initial value of the solvent flow rate, which may be chosen by performing a sensitivity analysis on a single pass RD column, as shown in our previous work [11]. Also, set a maximum value of the temperature (say θ) that can be allowed on the reactive stages, which is the temperature beyond which deactivation of the catalyst occurs. The converged process flow sheet with these initial values of the variables constitutes the base case. Go to step 2.

The process configuration used in Fig. 1 was obtained in a sequential way, as follows:

(i) Starting with a small RD column with four reactive stages (described in our previous work [33]), the simulation results were used to initialize taller columns. The unreacted gases are not recycled to the RD column in this step. The locations of syngas and solvent feed are trivial as they enter the bottom and top of the RD column, respectively.

(ii) In the next step, a taller column is simulated with the required number of stages to hold the desired amount of catalyst. The catalyst was equally distributed on the stages so that each stage contained a defined quantity of catalyst.

(iii) In this step, the unreacted gases are recycled to any stage in the RD column. The recycle stream can be fed to the bottom of the column as a trivial solution to start with, and the optimum location is obtained using the design algorithm.

Step 2: Change the feed location of the recycle gas stream, such that the overall methanol production in the process is maximized. The overall methanol production is the amount of methanol in the crude methanol stream shown in Fig. 1. Perform a sensitivity analysis and choose the location which maximizes the overall methanol production. Examine the column profiles. In this algorithm, "profiles" refers to the temperature and methanol production rate profiles. From the temperature profile, it can be seen that the recycle location divides the column into two distinct sections - top and bottom. In any section, successive stages on which the two profiles do not align constitute a 'zone' for heat removal with side coolers. These zones signify stages on which chemical equilibrium limitations are present. Then, go to step 3. Else, if changing the recycle feed stage leads to either a lower steady state with low overall rate of methanol production or convergence issues, go to step 11. If chemical equilibrium limitations are absent in the column and the maximum temperature of the reactive stage(s) in the top section is less than θ, go to step 12.

Step 3: Decrease the temperature of the recycle gas feed stream if the maximum temperature of the reactive stages in the top section exceeds θ by 20 °C or more. Else, go to step 4. If equilibrium limitations are present in the top section, decreasing the temperature of the recycle gas stream usually leads to an increase in the methanol production. In this case, decrease the temperature of the stream in steps until a maximum in the

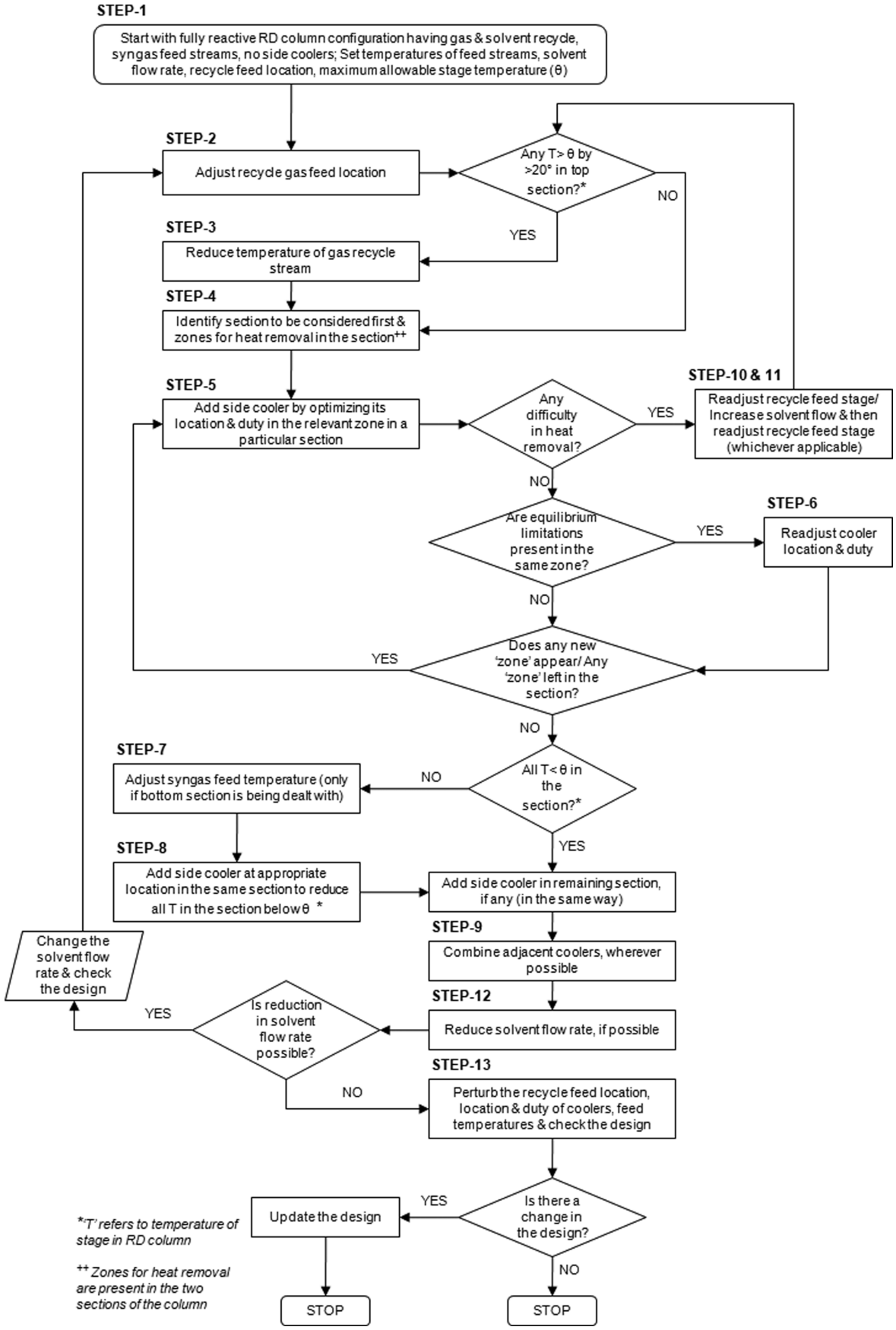

Fig. 3. Proposed design algorithm.

overall methanol production is obtained or the maximum temperature of the reactive stages does not exceed θ by more than 15 °C. Else, if a decrease in the temperature of the stream causes a decrease in the overall methanol formation, then decrease the temperature of the gas recycle stream until the maximum temperature of the reactive stage(s) in the top section does not exceed θ by more than 15 °C and go to step 4.

Step 4: The section in which a side cooler is to be added first is to be determined by trial and error. If putting coolers in the 'top section' first followed by the 'bottom' leads to difficulty in heat removal, then the bottom section is to be attempted first followed by the top. Else, if it is difficult to remove heat from either section, go to step 11. Difficulty in heat removal signifies the inability to remove heat from a given 'zone' by the side coolers. This happens for either of the following reasons: (i) simulation converging to a lower steady state as heat duty is increased or a cooler is placed at a particular stage, or (ii) problems associated with phase equilibrium and convergence issues.

Step 5: To add side coolers in zones for heat removal, determine the optimum location of a side cooler by putting a cooler with a small duty on each of the stages in a zone for heat removal and choosing the stage for which a maximum in overall methanol production is obtained. Then, gradually increase the cooling duty till a maximum in overall methanol production is reached. Observe the column profiles. If the two profiles align with each other for the section in question, repeat step 5 for the other 'section'. Else, if either chemical equilibrium limitations persist or a new zone for heat transfer appears in the same section, go to step 6. Else, if temperature of any stage in the same section is greater than θ, go to step 8. If equilibrium limitations are not present and the temperatures of all the stages are less than θ in both the sections, go to step 9. When difficulty in heat removal is faced by the addition of a side cooler, its location may be changed to an adjacent stage from the optimum and checked if the difficulty persists. If the difficulty persists, go to step 10.

Step 6: If chemical equilibrium limitations persist in the same zone, then either increase the duty of the existing cooler or shift the existing cooler to another stage above or below its present location, subsequently changing its duty. Choose the location and duty of the side cooler which maximizes the overall methanol production.

If a new zone appears in the same section after following step 5 and its location is close to an existing cooler (within 3-5 stages), then shift the existing cooler towards the new zone and change its duty in the same way. Else, if either the new zone is far, or changing the location and duty of the existing cooler does not help in removal of chemical equilibrium limitations, go to step 5. Check the column profiles. If the temperature of any stage in the same section is greater than θ, go to step 8. If the column profiles align after this step, repeat step 5 for the other section. If equilibrium limitations are not present and the temperatures of all the stages are less than θ in both the sections, go to step 9. In case of difficulty in heat removal, go to step 10.

Step 7: If the temperature of any stage in the top section is greater than θ, go to step 8. Else, for the bottom section, reduce the temperature of the syngas feed stream to its minimum allowable value first and check if the temperature of the stage(s) is still greater than θ. If the temperature is greater than θ, go to step 8. If reducing the temperature of the syngas feed stream creates difficulty in heat removal in step 8, eliminate this step (i.e., step 7) and go to step 8 directly. Check the column profiles. If the equilibrium limitations are not present and the temperatures of all the stages are less than θ in both the sections, go to step 9. Else, if equilibrium limitations are present in any section by appearance of a new zone for heat removal, go to step 5. Else, if the other section already has cooler(s), but some of its stages have temperatures greater than θ, go to step 8. In case of difficulty in heat removal, go to step 10.

Step 8: If the temperature of any stage is greater than θ in any of the sections, either increase the duty of the existing cooler, or change its position and duty such that either the overall methanol production is maximized or the decrease in methanol production from its previous value is minimum. Also, ensure that the temperatures of all the stages in that section are less than or equal to θ. If this step does not help in decreasing the temperature of the stage(s) below θ, add an additional cooler for the purpose. Do a sensitivity analysis by putting a cooler with a small duty on each of the stages (one at a time) in the area where stages require cooling and gradually increase the duty such that the temperature of the stages just drops to θ. In the process, it should not raise the temperature of any other stage to a value above θ. If that happens, repeat the procedure for a few stages above or below. If adding the cooler at either of the two or more locations gives the desired result, the optimum location must be such that either the overall methanol production is maximum or its decrease from the previous value is minimum. Check the column profiles. If equilibrium limitations are not present and the temperatures of all the stages are less than θ in both the sections, go to step 9. Else, if equilibrium limitations are present in any 'section', go to step 5. If the other 'section' already has cooler(s), but some of its stages have temperatures greater than θ after this step, repeat this step for that section. In case of a difficulty in the heat removal, go to step 10.

Step 9: If applicable, combine two adjacent coolers into one in any or both the sections. It is advised not to attempt to merge two coolers which are far apart from each other, i.e., placed apart by more than 5-6 stages. While merging coolers, only a particular section should be dealt with at a time and coolers from two different sections should not be merged. To merge a cooler, add a cooler with a duty equal to the greater of the two and check. If it does not create problems in heat removal due to any of the aforementioned reasons, increase the duty such that either the overall methanol production is maximized, or its change is minimum. If the temperature of any stage exceeds θ in this process, then do not combine the coolers and go to step 13. Else, if overall methanol production increases and a new zone appears, go to Step 5. If this step is not applicable, go to step 13.

Step 10: In case of difficulty in heat removal when adding coolers in any of the steps 4-7, move the gas recycle stream towards the

section in which the coolers are being currently added. This is because the recycle stream lowers the average temperature of the reactive stages in the given section and aids in heat removal. The recycle stream should not be moved more than 2-4 stages at a time. Problems with addition of the coolers are mostly faced in the 'bottom section' because of the high temperatures and shifting the recycle feed stream towards that section helps in removal of heat. Then, go to step 3. If the feed stage of the gas recycle is close to the respective end of the column by 5-7 stages after repetition of this step, and problems associated with heat removal persist, go to step 11.

Step 11: In case of difficulty in heat removal when either adding coolers or changing the location of the recycle feed in step 2, increase the solvent flow rate by about 10-15% of its current value and go to step 2. If no difficulty is faced during addition of the coolers, and favorable column profiles have been obtained after ensuring that chemical equilibrium limitations are removed so that all the (reactive) stage temperatures are less than θ, go to step 12.

Step 12: If chemical equilibrium limitations are absent in the column and the maximum temperatures of the reactive stages are less than θ, decrease the solvent flow rate by 5-10% and go to step 2. If further decrease of solvent flow rate is not possible, stop at the current solvent flow rate and go to step 13.

Step 13: Check if the recycle feed location can be changed to any stage above or below the present one, so that the overall methanol production increases further. If methanol production increases, update the recycle feed location. Also, check if the side coolers can be moved by a few stages above or below their present location and also if their duty can be either increased or decreased to increase the overall methanol production further. If the overall methanol production increases, update the current locations and duties of the coolers and go to step 14. Else, directly go to step 14. The coolers should be dealt with in the same order in which they were added to the RD column. Further, check if it is possible to further increase the overall methanol production by adjusting temperatures of any of the feed streams without raising the temperature of any stage in the column above θ. Temperature of a feed stream should only be changed until a maximum in methanol production is reached. The order in which the feed streams are to be dealt with is as follows: Gas recycle, Solvent feed, and Fresh syngas.

ILLUSTRATIONS: CASE STUDIES

A few design cases are given to demonstrate the proposed design methodology. Each case represents a different syngas composition that can be obtained from diverse sources: gasification of heavy residue, steam reforming and combined reforming of natural gas.

1. Case I

The molar percentages of CO, CO_2, H_2 and CH_4 in the syngas are 22.97, 6.86, 67.46 and 2.71, respectively. The flow rate of syngas is 2,290 kmol/h. This syngas has a H_2 : CO ratio of 2.94 and is similar to that obtained by combined reforming of natural gas, i.e., steam reforming followed by an oxygen-blown secondary reforming [34]. The steps of the design algorithm presented in section 3.3 are used in the design of the RD column as follows:

i. ***Step (1):*** A converged flow sheet as shown in Fig. 1 is used as the starting point. The stream summary for this converged flowsheet is shown in Table S1 in the supplementary information. The space velocity used is calculated according to the patent by Nemphos et al. [10] and is equal to 1.5 kg of catalyst per kmol/h of fresh syngas feed. The RD column has 44 reactive stages with catalyst loading of 43,382 kg equally distributed on all the stages. Non-reactive stages and side coolers are not present. Initially, the temperature of all the feed streams to the RD column is 200 °C, solvent flow rate is 120 kmol/h and the recycle gas stream is fed to the 40th stage. Fig. 4(a) shows the initial profiles of the RD column. The overall methanol production rate is 611.1 kmol/h. The maximum allowable temperature of reactive stage is 270 °C (θ).

ii. ***Step (2):*** The optimum stage for feeding the gas recycle stream is found to be 33, and increases the methanol production to 613.4 kmol/h. The profiles of the RD column are given in Fig. 4(b). Two sections, separated by stage 33, are present in the RD column with one zone for heat removal in each of the two sections. The zones extend from stage 1 to 15 in the top section and from stage 35 to 44 in the bottom section. Reduction of the temperature of the recycle gas stream is not required as the maximum temperature of the stages in the top section does not exceed θ by more than 10 °C. Hence, step (3) is not required and we can directly go to steps (4) and (5).

iii. ***Step (4):*** Coolers are first added at the top and then at the bottom. It is observed that this scheme does not cause any difficulty in heat removal and is hence followed.

iv. ***Step (5):*** The optimum location is found by adding a cooler with a duty of 0.25 MW as side heat duty in each of stages 5-14 and is identified to be stage 12. The overall methanol production increases to 614.5 kmol/h, and further to 633.7 kmol/h on increasing the cooling duty further to 6 MW. Further increase in the cooling duty decreased the methanol production. Fig. 4(c) shows the column profiles after this step. Equilibrium limitations are not completely removed because the methanol production rate (per stage) does not increase from stage 12 on moving downwards along the column. Rather, it shows a decrease on stage 14 and then increases. Hence, we go to step (6). A new zone for heat removal is also present in the top section (stages 1-8).

v. ***Step (6):*** The side cooler on stage 12 is relocated to stage 14 to further increase the overall methanol production to 634.3 kmol/h. However, the duty is not changed as increasing or decreasing the cooling duty from 6 MW decreases the overall methanol production. The column profile after this step is shown in Fig. 4(d). The new zone between stages 1 and 8 persists. But an additional cooler is not used since significant increase in the overall methanol production is not observed by doing so. At the end of this step, the temperatures of all stages in the top section are less than 270 °C and the equilibrium limitations are also removed, except on stages 2 to 8. Hence, step (5) is repeated for the bottom section.

vi. ***Step (5):*** The optimum cooler location and duty in the bot-

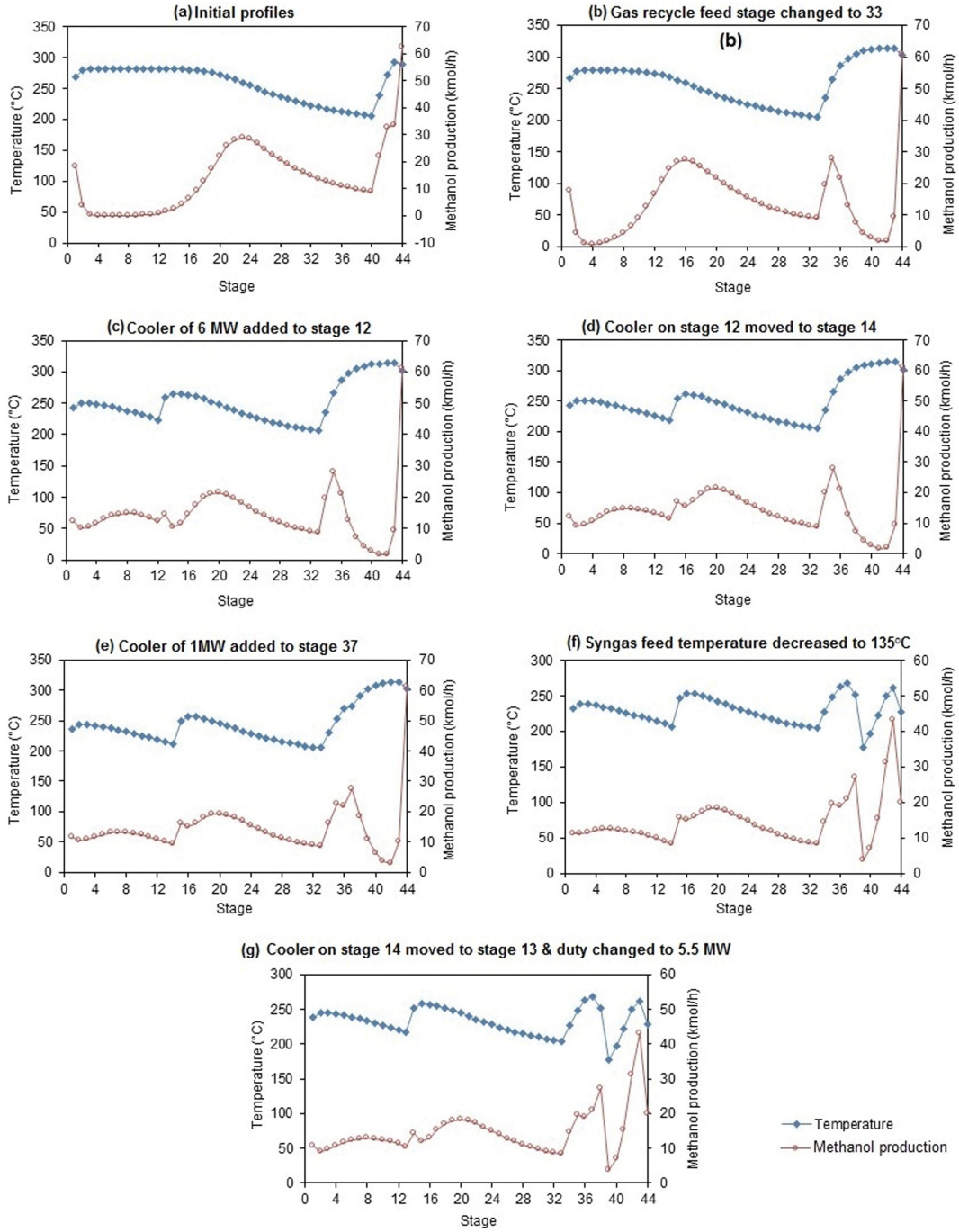

Fig. 4. Temperature and methanol formation profiles of RD column for Case-I.

tom section are found to be stage 37 and 1 MW, respectively. This was determined in a similar way as in the 'top section'. The overall methanol production increases to 636 kmol/h. The RD column profiles are as shown in Fig. 4(e). But the temperatures of stages 38-44 are much greater than 270 °C, the maximum being 313 °C for stage 43. Hence, step (7) is followed next.

vii. ***Step (7):*** The temperature of the fresh syngas stream is decreased to 135 °C, which is the temperature at the exit of the syngas compressor. The overall methanol production is 636.1 kmol/h. The maximum temperature of the reactive stages drops from 313 °C for stage 43 to 308 °C for stage 42. After this, it is found that moving the cooler on stage 37 to stage 39 and increasing the cooling duty to 3.7 MW brings about the desired change. The overall methanol production is 636.2 kmol/h. The updated column profile is as shown in Fig. 4(f). Steps (7)-(9) are not applicable here. So, step (11) is followed next.

viii. ***Step (11):*** The solvent flow rate is reduced to 100 kmol/h. However, difficulty in putting a side cooler in the 'bottom

section' was encountered, so the solvent flow rate was changed to 120 kmol/h. Step (11) is not applicable in this case and, therefore, step (13) is followed next.

ix. ***Step (13):*** It was found that the current gas recycle feed location (stage 33) is optimum and cannot be changed. While moving it to stage 34 decreased the overall methanol production, changing it to stage 32 resulted in convergence to a lower steady state with an overall methanol production of 538 kmol/h, which is not desired. Therefore, step (13) is followed next. The location and duty of the cooler in the 'top section' is further optimized to stage 13 and 5.5 MW, respectively, while those for the cooler in the bottom section cannot be changed as they are already at an optimum. An attempt to shift the location of the latter results in lower overall methanol production as the cooler is shifted to stage 38. When the cooler is moved to stage 40, the temperature of some stages in the 'section' exceeds 270 °C even though the methanol production increases. The cooler in the 'top section' was optimized first since it was added to the column before the one in the 'bottom section'. The overall methanol production is 637.5 kmol/h after this step. The column profile is given in Fig. 4(g). The maximum stage temperature is 269 °C and is observed for stage 37. After this step, we go to step (14). Increasing the temperature of the solvent stream brings about negligible change in the overall methanol production. The temperature of the fresh syngas feed stream is kept unaltered, as decreasing it reduces the methanol production, while increasing it or the temperature of the gas recycle stream raises the temperatures of some stages in the bottom section beyond 270 °C. It is found that a marginal increase in the overall methanol production (~0.04 kmol/h) takes place when the temperature of the solvent fed stream is increased to 207 °C. However, this is

Table 2. Summary of steps of design algorithm followed for Case II

S. No.	Step No. of proposed algorithm	Description/Changes made	Methanol production after the step (kmol/h)	Illustration of profiles
i.	1	Initial parameters- No. of stages: 44 Total catalyst loading: 43,382 kg (evenly distributed on stages) Solvent flow rate: 140 kmol/h Temperatures of feed streams (syngas/solvent/recycle): 200 °C Maximum allowable stage temperature: 270 °C	635.9	-
ii.	2	Gas recycle feed at stage 26	641.2	Fig. 5(a)
iii.	3	Gas recycle temperature decreased to 180 °C	649.7	-
iv.	4	This step could not be implemented	649.7	-
v.	10	Recycle gas feed location changed to stage 30	651.5	-
vi.	3	Gas recycle temperature decreased to 175 °C	652.9	-
vii.	4	The bottom section is to be dealt with first when adding coolers.	-	-
viii.	5	Cooler (SCB) of duty 0.5 MW added to stage 36 in the bottom section	655.1	Fig. 5(b)
ix.	7	Syngas feed temperature decreased to 137 °C	656	-
x.	8	SCB is moved to stage 39 and its duty increased to 3.32 MW	658.9	Fig. 5(c)
xi.	5	Cooler (SCT-1) of 4.5 MW added to stage 8 in the top section	678.5	Fig. 5(d)
xii.	6	Relocating SCT-1 does not help remove equilibrium limitations	678.5	-
xiii.	5	Another cooler (SCT-2) of duty 3 MW added on stage 15 in the top section	687.9	Fig. 5(e)
xiv.	6	SCT-2 is relocated to stage 18 and its duty changed to 3.1 MW	688.5	Fig. 5(f)
xv.	6	SCT-1 is relocated to stage 11 without any change in its duty	691	Fig. 5(g)
xvi.	8	Cooler on stage 39 in bottom section is moved to stage 38 without changing its duty	690.6	-
xvii.	8	SCT-2 is relocated to stage 19 and its duty changed to 3.5 MW	691.3	Fig. 5(h)
xviii.	6	SCT-1 is relocated to stage 12 and its duty increased to 4.5 MW	691.4	Fig. 5(i)
xix.	9	Merging of SCT-1 and SCT-2 is not possible	691.4	-
xx.	11	Reduction of solvent flow rate is not feasible	691.4	-
xxi.	13	Gas recycle feed stage cannot be changed. SCB cannot be optimized further. Changing temperatures of feed streams is not possible.	691.4	-

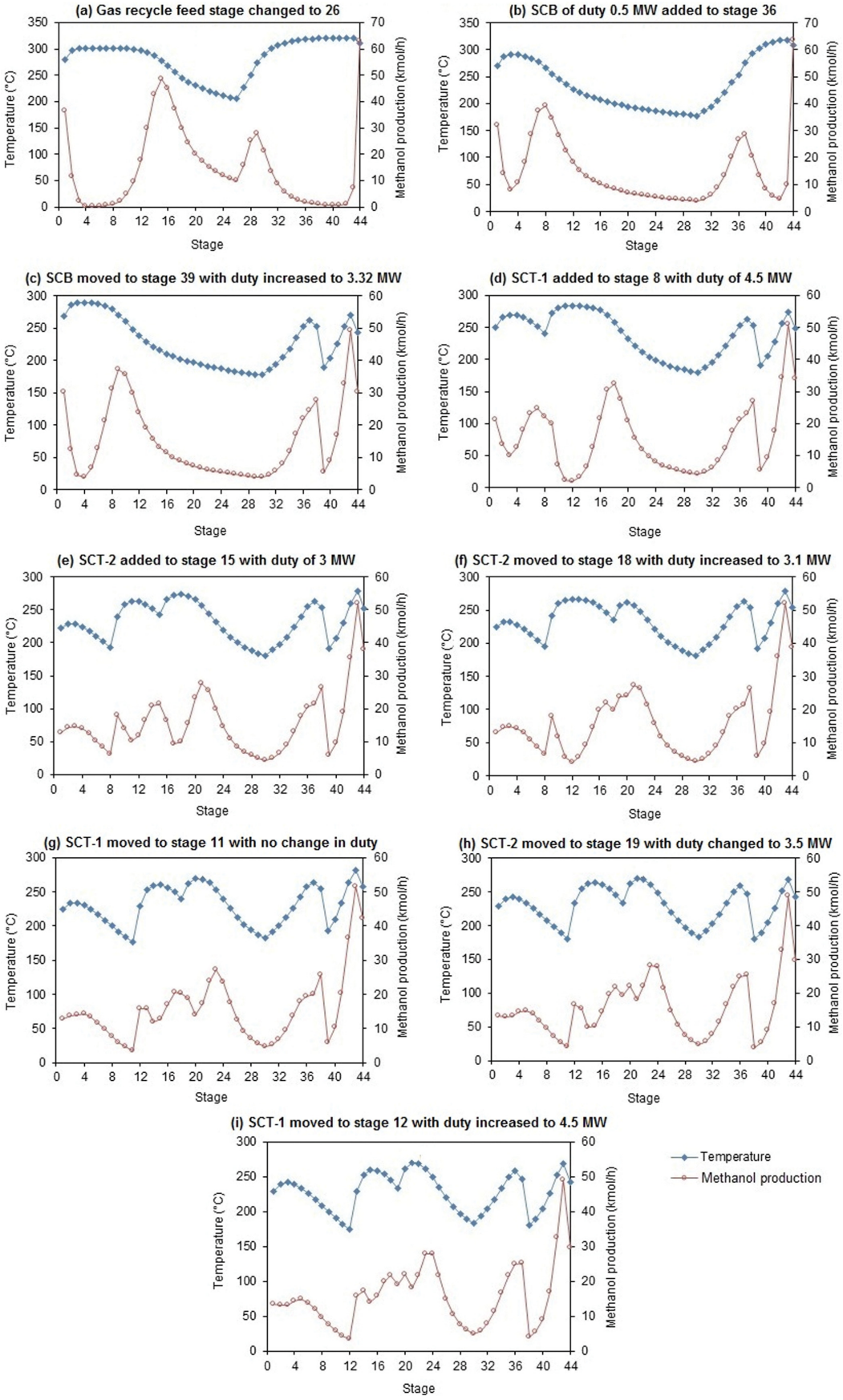

Fig. 5. Temperature and methanol formation profiles of RD column for Case-II.

not done here because of the small change. The column configuration obtained in (ix) is considered as the final design; the corresponding final parameters are shown in Table 4.

2. Case II

This syngas has composition similar to that obtained by gasification of heavy residue [34]. The molar percentages of CO, CO_2, H_2 and N_2 are 27.7%, 4%, 67.8% and 0.5%, respectively, with a H_2 : CO ratio of 2.45. The flow rate of syngas is 2,290 kmol/h. Table 2 summarizes the steps followed in the proposed design algorithm and the profiles at the end of the important steps are shown in Fig. 5. The detailed description is given in section S2 of the supplementary information. The final design parameters corresponding to this case are given in Table 4.

3. Case III

The fresh syngas composition used in this case is similar to that obtained by steam reforming of natural gas [34] and consists of 16.8% CO, 7.3% CO_2, 72.1% H_2 and 3.8% CH_4 with a H_2 : CO ratio of 4.3. Table 3 summarizes the steps followed in the proposed design algorithm and the profiles at the end of the important steps are shown in Fig. 6. The detailed description is given in section S2 of the supplementary information. The final design parameters corresponding to this case are given in Table 4.

Table 3. Summary of steps of design algorithm followed for Case III

S. No.	Step No. of proposed algorithm	Description/Changes made	Methanol production after the step (kmol/h)	Illustration of profiles
i.	1	Initial parameters- No. of stages: 44 Total catalyst loading: 43,382 kg (evenly distributed on stages) Solvent flow rate: 140 kmol/h Temperatures of feed streams (syngas/solvent/recycle): 200 °C Maximum allowable stage temperature: 270 °C	539.7	-
ii.	2	Gas recycle feed at stage 35	540.9	Fig. 6(a)
iii.	4	The top section is to be dealt with first when adding coolers		
iv.	5	Cooler of duty 5 MW is added to stage 14 in the top section	541.2	-
v.	6	Cooler on stage 14 relocated to stage 13 and its duty increased to 5.2 MW	544.3	Fig. 6(b)
vi.	5	Cooler of duty 0.75 MW added to stage 38 in the bottom section	544.6	Fig. 6(c)
vii.	7	Syngas feed temperature decreased to 134.8 °C	544.6	-
viii.	8	Cooler on stage 38 relocated to stage 41 and its duty increased to 2.55 MW	544.7	-
ix.	11	Reduction of solvent flow rate is not found to be feasible	544.7	-
x.	13	Changing recycle gas feed location is not possible. Location and duties of existing coolers cannot be optimized further. Solvent feed temperature is decreased to 60 °C.	544.7	Fig. 6(d)

Table 4. Optimum design parameters of all the cases obtained by the proposed design algorithm

	Case-I	Case-II	Case-III	Case-I_Alt
H_2: CO in syngas feed	2.94	2.45	4.29	2.94
Stoichiometric number of syngas feed*	2.03	2.01	2.69	2.03
Overall methanol production (kmol/h)	637.5	691.4	544.7	637.8
Design parameters:				
Recycle gas feed stage	33	30	35	27
Solvent flow rate (kmol/h)	120	140	140	200
Fresh syngas feed temperature (°C)	135	137	135	135
Solvent feed temperature (°C)	200	200	60	211
Recycle gas feed temperature (°C)	200	175	200	203
Cooler-1 stage/duty (MW)	13/5.5	12/4.5	13/5.2	12/3.45
Cooler-2 stage/duty (MW)	39/3.3	19/3.5	41/2.55	36/1.5
Cooler-3 stage/duty (MW)	-	38/3.32	-	41/2.73

Syngas flow rate, catalyst loading and total number of stages are same in all the cases.

*Stoichiometric number is the molar ratio of (H_2-CO_2) to (CO+CO_2) in syngas feed

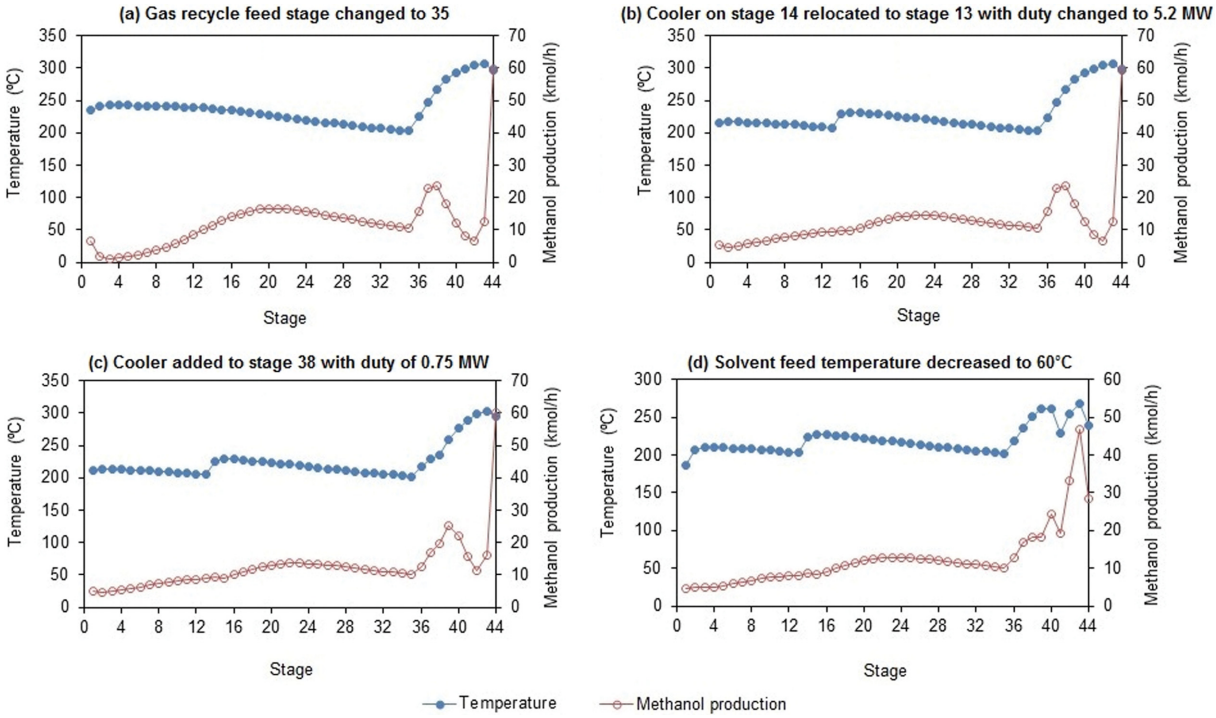

Fig. 6. Temperature and methanol formation profiles of RD column for Case-III.

The optimized variables of all the cases are given in Table 4. Case-I_Alt given in Table 4 refers to an alternative design of Case-I with a higher solvent flow rate and is discussed further in section 9. Chemical equilibrium limitations were not found to be present on the reactive stages of the optimized column configuration and a brief account of this has been provided in section S2.3 of the supplementary information.

COMMENTS ON THE INITIAL SOLVENT FLOW RATE AND TEMPERATURES OF THE FEED STREAMS

Minimizing the solvent feed rate in the RD column is one of the objectives of this work. However, it is necessary for the solvent flow rate to be kept high initially and then decreased in steps till the minimum feasible solvent flow rate is reached. A value of solvent flow lower than this minimum feasible value poses difficulties in heat removal in the side coolers. Another important aspect of starting from a higher solvent flow is that it helps to determine the section from which heat is to be removed first, as pointed out in (iv) of Case II. A lower solvent flow rate is disadvantageous as it leads to difficulty in decision-making by the designer. One has to decide if the difficulty in heat removal is due to a solvent flow rate lower than the minimum feasible value or due to a wrong choice of sequence of column sections (top/bottom) for heat removal.

Initially, the temperatures of the feed streams are also high. It is recommended to reduce the temperature during the course of the design. Starting from a low feed temperature often leads to convergence issues when attempts are made to increase it during the design exercise. There is also a possibility of obtaining a lower rate of overall methanol production if the initial feed temperatures are low. This is due to the wide difference observed in the stage temperatures in some cases.

COMPARISON WITH THE CONVENTIONAL PROCESS

To compare the performance of the RD based process for the studied cases, a flow sheet with a packed bed reactor (PBR) is simulated; a schematic is shown in Fig. S4 in the supplementary information. The PBR is simulated as a multi-tubular reactor with the "RPlug" module and operates at 50 bars. There are 2654 tubes in the reactor with length and diameter of 12 m and 0.04 m, respectively. The reactor is loaded with excess catalyst (40 MT) having a density of 2,000 kg/m^3 and a void fraction of 0.5 [35] such that chemical equilibrium is established. The methanol synthesis in the PBR is modeled using the kinetic model of Bussche and Froment [36]. In the PBR, the heat of reaction is utilized to generate steam at 42 bars, which is the practice in conventional Lurgi reactors [37]. Accordingly, the reactor is modeled with a constant medium temperature of 254 °C, similar to the work of Luyben [35]. A comparison of the performance of the conventional and RD-based processes is given in Table 5.

The per pass conversions of CO and H_2 and overall methanol production are comparatively higher for RD than the PBR in every case. However, the performance of RD in Case III is far superior to the other cases. This may be attributed to the high proportion of H_2 in the fresh syngas fed to the process. Syngas obtained by steam reforming of natural gas needs to be balanced to a stoichiometric ratio [37] (molar ratio of (H_2-CO_2) to (CO+CO_2)) of 2 *via* water gas shift reaction separately to obtain optimal performance

Table 5. Comparison of the performances of conventional (PBR-based) and RD-based processes

Performance metrics	Case I (H_2 : CO=2.9)		Case II (H_2 : CO=2.5)		Case III (H_2 : CO=4.3)	
	PBR	RD	PBR	RD	PBR	RD
Per pass reactant conversions (%):						
CO	26.0	43.9	33.77	55.5	32.7	86.2
CO_2	9.4	8.9	8.96	7.6	30.3	54.1
CO & CO_2 (combined)	19.27	24.74	26.63	34.19	31.96	73.22
H_2	13.02	16.8	17.23	22.8	5.3	6.1
Overall reactant conversions (%):						
CO	94.6	97.5	96.1	98.4	96.0	99.7
CO_2	78.0	80.6	71.4	78.5	94.8	98.3
CO & CO_2 (combined)	90.74	93.6	93.01	95.38	95.67	99.26
H_2	88.1	91.0	91.2	93.6	73.5	76.3
Overall methanol production (kmol/h)	617.3	637.5	673.6	691.4	524.0	544.7
Incremental production increase by RD (%)	3.2		2.6		3.9	

in a PBR. This step is, however, not required in the case of the RD-based process since it is capable of giving higher conversions and methanol production without balancing the feed.

OPTIMALITY OF THE SOLUTION OBTAINED WITH THE PROPOSED DESIGN ALGORITHM

The optimality of the solution obtained with the design algorithm is one of the important factors to determine its usefulness. As indicated in the introduction, the mathematical optimization of this problem requires the solution of an MINLP formulation, which may be computationally expensive because of the following reasons:

- All the design variables are optimized simultaneously, which requires searching in a large space.
- The presence of a recycle stream, the non-linear mass and energy balances and the phase equilibrium calculations (involving non-condensables) make the calculations complex.

The solution of the mathematical optimization problem, therefore, requires a very good initial guess. Else, this may result in an infeasible solution or lead to multiple steady states (discussed in section 8). Therefore, continuous monitoring and intervention by the designer is required when resorting to mathematical optimization techniques. The developed design algorithm tends to simplify the approach by optimizing one variable at a time, followed by checking if further improvements are possible. It is also iterative in nature and may resort to repetition of steps if any criterion is not satisfied. It helps the designer decrease the search space and also monitors the course of the solution simultaneously. Optimization of a once-through RD column for methanol synthesis was performed in our earlier work [11], and it was observed that multiple optima are present due to the non-linearity of the problem. Since the solution is strongly dependent on the choice of initial values for the design variables, obtaining the global optima can neither be guaranteed for the mathematical optimization nor the design algorithm. Therefore, a multi-parameter sensitivity analysis is carried out for Case-I in order to ensure that at least a local optimum is reached by following the algorithm. The variables - temperatures of the feed streams, duties of the side coolers, and the solvent flow rate - are varied by ±5% of their optimal values. The locations of the side coolers and the gas recycle feed were varied by one stage above and below their optimal locations. The optimum design variables for Case-I are given in Table 4, and the ranges in which the variables are checked in the sensitivity analysis are shown in Table

Table 6. Range of design parameters used in the multi-parameter sensitivity analysis for Case-I

Design parameters	Optimum values	Range used in sensitivity analysis
Recycle gas feed stage	33	32-34
Solvent flow rate (kmol/h)	120	114-126
Fresh syngas feed temperature (°C)	135	128.5-142.1
Solvent feed temperature (°C)	200	190-210
Recycle gas feed temperature (°C)	200	190-210
Cooler-1 stage	13	12-14
Cooler-1 duty (MW)	5.5	5.23-5.78
Cooler-2 stage	39	38-40
Cooler-2 duty (MW)	3.3	3.14-3.47

6. Though a combination of all the variables leads to a large number of cases, some of them are infeasible and cannot be converged. Based on the results from the sensitivity analysis (Fig. S3 in the supplementary information), it can be concluded that the rate of overall methanol production obtained by the design algorithm is optimal. Additionally, a non-linear programming (NLP) problem was also solved to obtain the maximum methanol production in the process. It was observed that different sets of initial guesses led to similar solutions and the maximum methanol production obtained using the proposed design methodology was found to be within 0.2% of the solution of the NLP. A more detailed discussion is provided in section S3 of the supplementary information.

MULTIPLE STEADY STATES (MSS)

Multiplicity of steady states in RD has been reported for synthesis of fuel additives, methyl *tert*-butyl ether (MTBE) [38] and *tert*-amyl methyl ether (TAME) [39,40] as examples. The MSS behavior is attributed to the interaction between chemical reaction and simultaneous separation, which may lead to a great extent of non-linearity [41]. A detailed review on non-linear dynamics and analysis of MSS in RD has been presented by Kienle and Marquardt [42]. MSS in gas-to-liquid RD processes have been reported earlier for Fischer-Tropsch (FT) synthesis by Srinivas et al. [43] and have also been observed for methanol synthesis from syngas in the present study. For RD in FT synthesis, MSS were observed by varying the condenser temperature for a once-through conversion. In the present study, MSS were observed when the temperature or feed location of the gas recycle stream to the RD column, or the duty of the side coolers was changed. Fig. 7(a) shows the effect of varying the temperature of the recycle gas feed from 190 °C to 202 °C on the methanol production rate and the existence of MSS in the range of 196-198 °C. The feed stage of the same stream is varied and its effect on the overall methanol production rate is shown in Fig. 7(b). In this case, MSS are observed for stages 24-26 as the feeding locations. Note that MSS are also possible for methanol synthesis in a once-through RD column, and multiplicity in solutions was observed when varying the reflux ratio in the column. The causes may be attributed to a combination of factors which lead to MSS in either a continuous stirred tank reactor or a non-reactive distillation column: reaction kinetics, heat effects, VLE, effect of energy balance on compositions, singularities of mass-molar relationships for input variables [44]. A more detailed investigation is required to determine the cause of MSS in the present study and may be considered as future work. The knowledge of the existence of MSS is essential when designing the RD column, and the designer should be aware of this so that the branches with lower production rates can be avoided while implementing the proposed algorithm. The existence of MSS is a very crucial factor during the start-up of the process, and it is always desired to start with the branch having higher methanol production rate to avoid loss of productivity of the process and maintain high conversions of reactants. Therefore, it is desirable to choose operating conditions conducive to the branch corresponding to higher methanol production.

ECONOMIC CONSIDERATIONS

Though it is possible to develop a design with the minimum solvent flow rate using the proposed methodology, the cost of the column is also an important consideration to bear in mind. Hence, a study was conducted to evaluate the effect of the solvent flow rate on the cost of the RD columns designed for the syngas composition used in Case-I. Initially, the solvent flow rate was taken as 200 kmol/h and was gradually decreased in steps till 120 kmol/h, as shown in Case-I. A lower solvent flow shifts the location of the recycle gas feed further down along the column. This leads to a larger diameter for a greater fraction of the column height and hence, higher capital costs. This dependence is shown in Fig. 8 for Case-I. The costs of the designed RD columns were determined with Aspen Process Economic Analyzer V8.4 using 2013 as the base year for costing. It is seen that the cost of the column increases by 24% and 44% as the solvent flow rate is decreased to 160 kmol/h and 120 kmol/h, respectively, from the initial value of 200 kmol/h. The RD column configuration designed at 200 kmol/h was used in our work on economic analysis of RD for methanol synthesis [14] because of its lower capital cost, and the economics of the RD-based process vis-à-vis the conventional one can be found there.

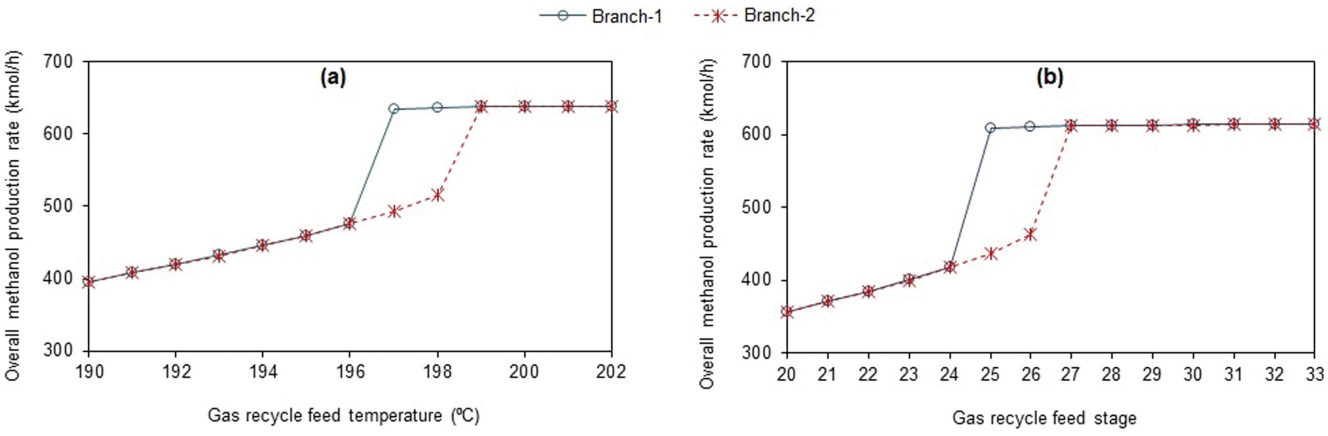

Fig. 7. Multiple steady states in Case-I (a) for different recycle gas feed temperatures and (b) for different recycle gas feed locations.

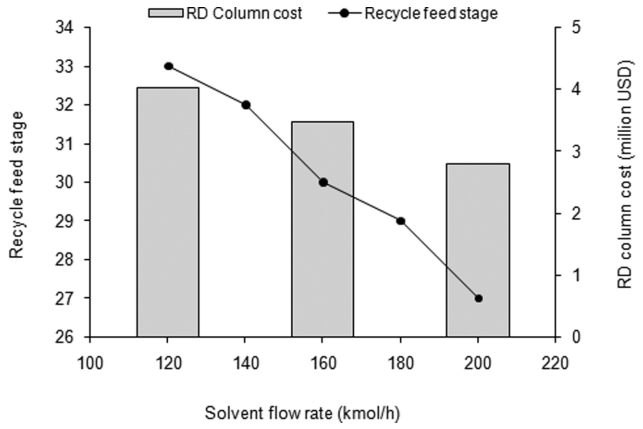

Fig. 8. Dependence of the recycle gas feed location and cost of the RD column on the solvent flow rate.

The optimum design parameters of this case, referred to as Case-I_Alt, are given in Table 4. It is noteworthy that both the configurations at 120 kmol/h and 200 kmol/h have comparable performance in terms of the methanol production and the conversions of reactants. Case-I_Alt has three side coolers instead of two in Case-I. However, the greater number of coolers does not significantly increase the capital cost. The capital cost of the coolers increases by only 5.6% (~0.03 million USD) due to the additional cooler when the solvent flow rate is increased to 200 kmol/h from 120 kmol/h. It is important to mention that Case-I_Alt can be designed with a total of two coolers instead of three. The two coolers in the bottom section can be merged into a single unit on stage 38 (step 8); however, doing so decreases the overall methanol production to 635.8 kmol/h. Therefore, the designer needs to decide on the solvent flow rate based on the capital cost of the column when the performance for different configurations is identical like in Case-I and Case-I_Alt.

CONCLUSIONS

A simulation-based design methodology for methanol synthesis by RD was developed in the present work and is demonstrated for three different syngas compositions. The proposed design algorithm aims to maximize methanol production, while simultaneously minimizing the number of side coolers and solvent input to the RD column. The performance of the designed RD column configuration in each case is compared with the conventional process scheme. It is seen that the performance of the RD-based process is either comparable to, or better than, the conventional one for all the cases. The optimality of the solution obtained by the developed design algorithm is also evaluated for one of the cases to ensure that a local optimum is reached. It is seen that the solution is very close to a local optimum and within 0.3% of it. It was also shown that the capital cost of the RD column is dependent on the solvent flow rate and the economics should be considered when there are multiple solutions with respect to the solvent flow rate. For the conventional Cu-ZnO-Al_2O_3 catalyst used in this work, it was observed that higher hydrogen content in the fresh syngas feed led to better performance of RD relative to the conventional process.

Although the current work proposes a reactor (RD column) that is different from reactors or RD column in practice, the hardware required is not particularly new and is well known in chemical plant operations. For example, the catalyst may be in the form of structured packing [28] and the side coolers used on particular stages may be used in practice as pump-arounds (as in crude distillation columns) with heat exchangers. Therefore, the equipment is not particularly new in terms of operation and maintenance.

Although it has been shown in this work that an optimal RD column configuration can be obtained by the proposed methodology, it may also be interesting to use a hybrid method that combines both the proposed methodology and MINLP in future work; the solution obtained from the design methodology can be used as an initial guess for the solution of the MINLP. Production of methanol from CO_2 is looked upon as a sustainable process and can bring out the potential of RD for methanol synthesis when a catalyst with high activity [45] or an alternate solvent [46] is used due to the ability of RD to separate the products (methanol and water) *in situ*. Therefore, it would be interesting to design an RD column to produce methanol from CO_2 with suitable VLE and kinetic models using the algorithm proposed in this work.

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NOMENCLATURE

(MI)NLP : (mixed integer) non linear programming
PBR : packed bed reactor
RD : Reactive distillation
VLE : vapor liquid equilibrium

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Reactive distillation for methanol synthesis: Simulation-based design methodology

Shashwata Ghosh and Seethamraju Srinivas†

Department of Energy Science and Engineering, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India
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S1. Stream Data for Starting Point of Case I

The compositions, flow rates, temperatures and pressures of the streams of the flowsheet shown in Fig. 1 for step (1) of Case I are given in Table S1.

S2. Steps for Cases II and III and Comments on Removal of Chemical Equilibrium Limitations

S2-1. Case II

The order in which the steps of the design algorithm are used is given in the following description:

i. ***Step (1):*** To start with, the RD column has 44 stages and a total catalyst loading of 43,382 kg in accordance with the space velocity specified in Case I. The column is fully reactive and the catalyst is distributed evenly on 44 stages. The initial solvent flow rate is 140 kmol/h and the temperatures of all the feed streams - solvent, gas recycle and fresh syngas are 200 °C. The maximum allowable temperature of the reactive stages is 270 °C. Initially, the overall methanol production rate is 635.9 kmol/h.

ii. ***Step (2):*** The optimum gas recycle feed location is stage 26 and the overall rate of methanol production increases to 641.2 kmol/h after this step. The corresponding RD column profile is shown in Fig. 5(a). Initially, there are two sections on either side of stage 26 with one zone for heat removal in each of the sections- stage 1 to 15 in the 'top section' and the stage 29-44 in the 'bottom section'. The maximum temperature in the 'top section' is ~31 °C higher than the minimum allowable stage temperature of 270 °C. Hence, we go to step (3).

iii. ***Step (3):*** Temperature of the gas recycle stream is now reduced in steps from 200 °C to 180 °C, resulting in an increase in the overall methanol production rate to 649.7 kmol/h. Reducing the temperature of the stream below 180 °C results in convergence to a lower steady state with an overall rate of methanol production of 317.2 kmol/h. The maximum stage temperature in the top section now reduces to 289 °C (stage 3). This is followed by steps (4) and (5).

iv. ***Step (4):*** In this problem (Case II), it is observed that the heat removal from the bottom section followed by the 'top section' is feasible. Hence, heat removal from the bottom section is attempted first *(This was determined by doing the design exercise for a solvent flow rate of 160 kmol/h before this case with 140 kmol/h. The design exercise with a solvent flow rate of 160 kmol/h is not shown here - however, it helped to determine the feasible sequence of column 'sections' for heat removal.).*

v. ***Step (5):*** In this step, the optimum stage for heat removal is found to be 33. However, problems in phase equilibrium calculation were faced on increasing the cooling duty and therefore, this step cannot be completed. So, we move on to step (10).

vi. ***Step (10):*** The recycle gas feed location is moved down from stage 26 to stage 30 since problems in heat removal were

Table S1. Stream data for step (1) of Case I

	Units	Bottom product (solvent) recycle	Recycle gas	Syngas feed	Crude methanol	Purge	Fresh solvent (make up)	Vapor from column
Mole fractions								
CO		0.03	0.11	0.23	0.00	0.11	0	0.10
CO_2		0.02	0.09	0.07	0.01	0.09	0	0.09
H_2		0.07	0.60	0.67	0.00	0.60	0	0.58
CH_4		0.01	0.19	0.03	0.00	0.19	0	0.18
CH_3OH		0.02	0.01	0	0.82	0.01	0	0.04
H_2O		0.00	0.0009	0	0.17	0.00	0	0.01
Squalane		0.86	0.0005	0	0	0.00	1	0.00
Mole flow	kmol/h	140	15,761.8	2,290	741.48	321.7	0.16	16,824.9
Temperature	°C	288	200	200	40	40	30	269
Pressure	bar	52	52	52	50	50	50	50

faced in the bottom section of the column. The overall rate of methanol synthesis now increases to 651.5 kmol/h. The maximum stage temperature in the 'bottom section' drops to 319.7 °C on stage 43 from 321 °C on stage 42 (seen after the previous step). Then, we again go to step (3).

vii. ***Step (3):*** The temperature of the gas recycle stream is further reduced to 175 °C, resulting in an increase in the overall methanol production rate to 652.9 kmol/h. However, further decrease in the temperature of this stream is not possible because of the same reason as in (iii). Now, we again move to step (5).

viii. ***Step (5):*** In the bottom section, the optimum cooler location and duty are stage 36 and 0.5 MW, respectively. It is important to note that stages 37-44 still exhibit temperatures greater than 270 °C, peaking to 318 °C on stage 43. Equilibrium limitations also persist, as shown in the column profiles in Fig. 5(b). Step (7) is followed next to reduce the temperature as readjusting the location and duty of the cooler does not increase the methanol production rate.

ix. ***Step (7):*** To reduce the stage temperatures in the 'bottom section', the temperature of the fresh syngas feed stream is reduced to 137 °C - this is the temperature at which the stream exits the syngas compressor. The overall methanol production now increases to 656 kmol/h and the maximum stage temperature in the 'bottom section' drops to ~312 °C (stage 42) from ~318 °C (stage 43). This is followed by step (8).

x. ***Step (8):*** In this step, the cooler on stage 36 is first moved to the other stages in its vicinity and checked if it helps to reduce the temperatures of all the stages in the bottom section. It is found that moving the existing cooler to stage 39 and increasing its duty to 3.32 MW helps in achieving the desired objective. Also, it is now observed that the equilibrium limitations are not present in the 'bottom section' and all the stages in the section have temperatures less than 270 °C. The column profiles are shown in Fig. 5(c). Hence, we now go to step (5) and add coolers in the top section. The overall methanol production rises to 658.9 kmol/h after this step.

xi. ***Step (5):*** The optimum cooler location and duty of the cooler are stage 8 and 4.5 MW, respectively. The overall methanol production is 678.5 kmol/h. However, equilibrium limitations are present, as seen from the column profiles in Fig. 5(d). Hence, we go to step (6).

xii. ***Step (6):*** Relocating the existing cooler does not help remove equilibrium limitations, hence step (4) is repeated and a new cooler (SCT-2) is put in the top section. The existing cooler in the top section is labeled 'SCT-1'

xiii. ***Step (5):*** The optimum stage and duty of SCT-2 are 15 and 3 MW, respectively. The column profiles after this step are as given in Fig. 5(e). Though the overall methanol production increases to 687.9 kmol/h, it can be clearly seen that equilibrium limitations exist around SCT-2. Hence, step (6) is repeated.

xiv. ***Step (6):*** SCT-2 is relocated to stage 18 and its duty changed to 3.1 MW. This leads to an overall methanol production rate of 688.5 kmol/h. The profiles of the RD column after this step are given in Fig. 5(f). Equilibrium limitations still exist near SCT-1 and hence, step (6) is repeated.

xv. ***Step (6):*** SCT-1 is relocated to stage 11. However, duty of SC-1 is not changed since increasing it leads to a decrease in the overall methanol production. The column profiles obtained after this step are shown in Fig. 5(g). The overall methanol production now is 691 kmol/h. Further removal of the equilibrium limitations by using more coolers or relocating SCT-2 reduces the overall methanol production and is, therefore not useful. Though the temperatures of all the stages in the 'top section' are less than 270 °C, the temperature of stage 43 in the 'bottom section' exceeds this value. Hence, we go to step (7). Since the temperature of syngas feed stream has already been reduced to its minimum value and further reduction requires an additional heat exchanger, we go to step (6).

xvi. ***Step (8):*** The cooler in the 'bottom section' is moved to stage 38 which results in a reduction of the temperature of stage 43. However, the temperatures of stages 20-22 increase now and exceed 270 °C. The heat duty of the cooler is not changed as decreasing it leads to further rise in the temperature of stages 20-22. The overall methanol production rate is 690.6 kmol/h. Hence, step (8) is repeated for the 'top section'.

xvii. ***Step (8):*** SCT-2 is relocated to stage 19 and its heat duty is changed to 3.5 MW since it is closer to stages 20-22 than SCT-1. The overall methanol production now increases to 691.3 kmol/h. Instead of moving SCT-2 to stage 19, increasing its cooling duty to 3.9 MW without relocation also helps to reduce the temperatures of stages 20-22 below 270 °C. But, the overall methanol production rate drops to 689.7 kmol/h in that case and is, therefore, not used. The column profiles are given in Fig. 5(h). A new zone for heat removal can be observed between stages 12-18. Hence, step (6) is repeated next.

xviii. ***Step (6):*** Relocating SCT-1 to stage 12 and increasing its duty to 4.5 MW increases the overall methanol production rate to 691.4 kmol/h. If the cooling duty is increased further, the rate of methanol production increases further. However, the temperatures of stages 20 and 21 exceed 270 °C again, which is undesirable. Fig. 5(i) shows the column profiles after this step. After this step, all the stage temperatures are below 270 °C and the equilibrium limitations are also removed as far as possible. Since there are two coolers in the 'top section', the possibility of merging them into one common cooler is checked next in step (9).

xix. ***Step (9):*** Merging SCT-1 and SCT-2 into a single unit is not possible as it causes problems in phase equilibrium calculations and leads to convergence issues. Hence, this step is not possible. We can now move on to step (11).

xx. ***Step (11):*** In this step, the solvent flow rate is reduced to 120 kmol/h since coolers could be installed and favorable column profiles are obtained for a solvent flow rate of 140 kmol/h. However, the lower solvent flow rate does not lead to a favorable design as this poses problems in heat removal and relocating the recycle stream i.e. step (9) also does not help. Hence, the solvent flow rate of 140 kmol/h is not changed. Step (13) is followed next.

xxi. ***Step (13):*** The gas recycle feed stage is not changed as chang-

ing it either reduces the overall methanol production rate or creates convergence problems associated with the phase equilibrium calculations. Since coolers in the top section are already adjusted in (xviii) and no other change was made to the RD column after that, it is checked if the cooler in the 'bottom section' can be adjusted. But, readjusting it creates calculation issues as the last step and hence, no change is made. Changing the temperatures of the feed streams is not done as decreasing the temperatures of the streams lowered the methanol production and increasing them led to elevated temperatures of some of the stages beyond 270 °C. Thus, the final design corresponds to the column configuration obtained after (xviii).

S2-2. Case III

The order in which the steps of the design algorithm are used is as follows:

i. ***Step (1):*** The initial values of all the temperatures of the feed streams, catalyst loading and distribution on the stages, recycle gas feed stage, and column configuration are the same as in Cases I and II. The initial solvent flow rate is 140 kmol/h. The overall rate of methanol production is 539.7 kmol/h. The maximum allowable reactive stage temperature is the same as in the other two cases.

ii. ***Step (2):*** The optimum feed location for the recycle gas stream is stage 35 and the corresponding overall methanol production is 540.9 kmol/h. The column profiles are given in Fig. 6(a). One zone for heat removal can be seen in each of the two sections of the column - stage 1 to 20 in the 'top section' and the stage 3-44 in the 'bottom section'. Since the maximum temperature of the stages in the top section is 247 °C, step (4) can be directly followed after this instead of step (3).

iii. ***Step (4):*** In this case, it is observed that coolers can be added in the top section first followed by the bottom section without any issues.

iv. ***Step (5):*** A side cooler is added in the top section. Its optimum location and duty are stage 14 and 5 MW, respectively. The overall methanol production rate increases to 541.2 kmol/h. However, chemical equilibrium limitations persist in this zone as the methanol production profile does not sharply increase similar to the temperature profile below the stage on which the cooler is located. Hence, step (6) is followed next.

v. ***Step (6):*** Relocating the cooler in the top section to stage 13 and increasing its duty to 5.2 MW further maximizes the overall methanol production rate and removes the equilibrium limitations. The overall methanol production rate is 544.3 kmol/h and the column profiles are given in Fig. 6(b). Though equilibrium limitations are present on stages 2-12, another cooler is not added since such an addition does not increase the rate of methanol production. Since the temperatures of all the stages in the top section remain below 270 °C, step (5) is followed for the bottom section.

vi. ***Step (5):*** For the bottom section, the optimum cooler location and duty are found to be stage 38 and 0.75 MW, respectively. The corresponding methanol production rate is 544.6 kmol/h. The column profiles are shown in Fig. 6(c) and the maximum stage temperature is 302 °C for stage 43. Hence, step (7) is followed next.

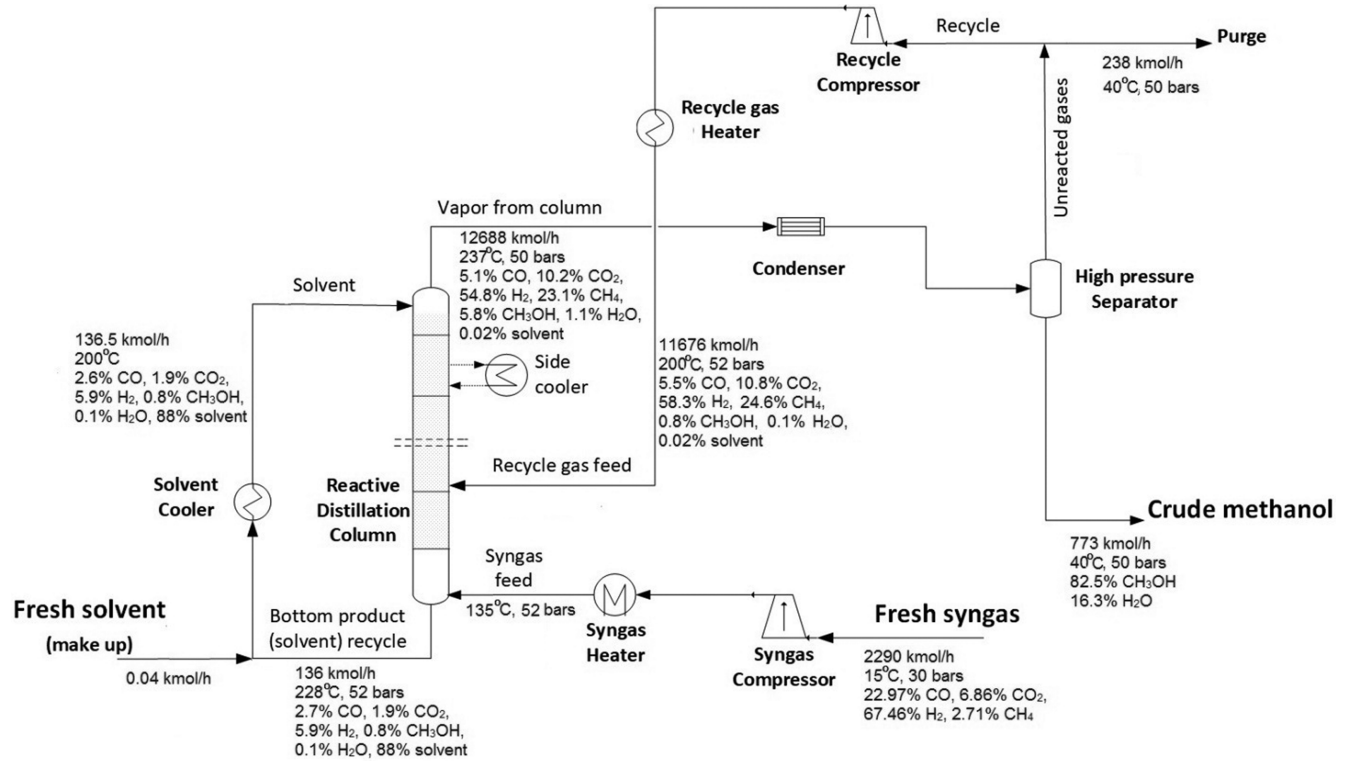

Fig. S1. Stream data for Case-I.

vii. ***Step (7):*** The temperature of the fresh syngas feed stream is reduced to 134.8 °C, which is the temperature at which the stream leaves the compressor. The overall rate of methanol production remains constant at 544.6 kmol/h and stage 43 has the maximum stage temperature of ~297 °C. Therefore, we go to step (8).

viii. ***Step (8):*** The cooler in the bottom section is relocated and its optimum location and duty are stage 41 and 2.55 MW, respectively. The overall rate of methanol production after this step is 544.7 kmol/h. Steps (9) and (10) are not applicable here. Hence, we go on to step (11).

ix. ***Step (11):*** Attempt is made to reduce the solvent flow rate to 120 kmol/h. However, this was not feasible as it led to difficulty in the heat removal and violation of the constraint on the maximum allowable stage temperature. Next, we go to step (13).

x. ***Step (13):*** It is checked whether the gas recycle feed stage can be changed. This is not possible as doing so reduces the overall methanol production rate. The present location and duties of the side coolers are found to be optimal and are not changed further. It is seen that the temperature of the solvent feed stream could be decreased to 60 °C without any change in the overall rate of methanol production. The overall rate of methanol production changes negligibly when the temperature of the gas recycle stream is increased and therefore, the temperature is not increased. The column profiles after this step are shown in Fig. 6(d). The final methanol production rate is 544.7 kmol/h and the profiles are shown in Fig. 6(d) - this design corresponds to the column configuration obtained after step (x).

S2-3. Process Stream Data of Final Design for Case-I

The flow rates and molar compositions of the streams for Case-I are shown in Fig. S1. The liquid phase composition profiles of the RD column for a similar case (Case-I_Alt) are given in our work on energy and economic analysis of RD for methanol synthesis [14].

S2-4. Removal of Chemical Equilibrium Limitations

Chemical equilibrium limitations are not found to influence methanol formation on the stages of the optimized column configuration. This has been shown in Fig. S2 for Case-I and shows a plot of the fractional approach to equilibrium (K/K_{eq}) on all the reactive stages of the optimized RD column configuration. The number indicates the fraction of chemical equilibrium attained on the stage

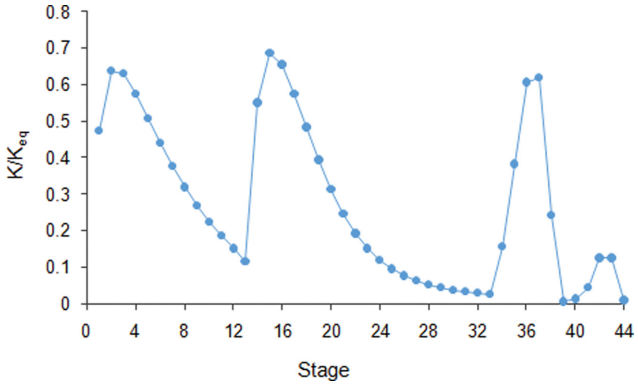

Fig. S2. K/K_{eq} profile of the optimized RD column for Case-I.

and is described in our previous work [12]. A value of K/K_{eq} equal to 1 suggests that chemical equilibrium is attained on a reactive stage and a value further away from 1 suggests that the reaction is kinetically controlled. From Fig. S2, it can be observed that a maximum of 0.7 i.e. 70% of the chemical equilibrium value is attained, and, therefore equilibrium limitations are non-existent in the optimized configuration. The values of the fraction drop remarkably at the stages, where the temperature drops, i.e. on which side coolers are used (13 and 39) and stage 33, which receives the gas recycle stream (which is at a lower temperature than the average column temperature).

S3. Optimality of Solution Obtained with the Design Algorithm: Some Observations from the Multi-parametric Sensitivity Analysis

It is difficult to provide a description of all the cases here. So, only a few important points are highlighted, which show the major reasons of difference between the optima obtained by the design algorithm and the sensitivity analysis:

(i) Decreasing the temperature of the recycle gas feed stream by 5% for any value of the other variables leads to a lower steady state, in which the overall methanol production rate is severely reduced. In some of the cases, a converged solution could not be reached.

(ii) In Fig. S3(a), the temperature of the fresh syngas feed stream and the duty of the side cooler in the bottom section are varied for different recycle gas feed locations, keeping the other variables constant at their optimal values given in Table 3. The

Table S2. Range of design parameters used in the multi-parameter sensitivity analysis for Case-I

Design parameters	Optimum values	Range used in sensitivity analysis
Recycle gas feed stage	33	32-34
Solvent flow rate (kmol/h)	120	114-126
Fresh syngas feed temperature (°C)	135	128.5-142.1
Solvent feed temperature (°C)	200	190-210
Recycle gas feed temperature (°C)	200	190-210
Cooler-1 stage	13	12-14
Cooler-1 duty (MW)	5.5	5.23-5.78
Cooler-2 stage	39	38-40
Cooler-2 duty (MW)	3.3	3.14-3.47

maximum methanol production rates are obtained on moving towards the lower bound of the side cooler duty (−3.1 MW) for stage 33 as the recycle gas feed stage. However, on decreasing the cooling duty from −3.3 MW to −3.1 MW, the temperature of the stages in the bottom section start increasing due to decreasing rate of heat removal and the constraint on maximum allowable reactive stage temperature is violated. Hence, the overall methanol production rate corresponding to the recycle feed stage 33, side cooling duty (bottom section) of −3.3 MW and fresh syngas temperature of 135.3 °C is optimal. A similar observation can be made in Fig. S3(b), which shows the variation in the overall rate of methanol production with fresh syngas feed temperature and side cooler duty (bottom section) for different values of the solvent flow rate, keeping other variables same as shown in Table 3. In this case, the overall methanol production rate corresponding to 120 kmol/h of solvent flow and side cooler duty (bottom section) of −3.3 MW and fresh syngas temperature of 135.3 °C is optimal despite higher rates of methanol production for cooling duty of −3.1 MW. This is because of the violation of the same constraint on maximum reactive stage temperature below cooling duty of −3.3 MW.

(iii) Fig. S3(c) shows the effect of fresh syngas feed temperature and side cooler duty (top section) on the overall rate of methanol production. The highest rates of methanol production are obtained for a solvent flow rate of 120 kmol/h and fresh syngas feed temperature of 142 °C, even though the optimum point obtained by means of the design variable is for a temperature of 135.3 °C. In this case, it is important to note that the temperature of 142 °C is attainable by the developed design algorithm (according to Step (14)). However, it is not used since the change in methanol production rate is insignificant. It is seen that the overall methanol production rate can be increased by only 0.08% by increasing the fresh syngas feed temperature to 142 °C, beyond which the constraint on maximum allowable stage temperature is violated.

(iv) Fig. S3(d) shows the change in overall methanol production rate with the change in the temperature of the fresh syngas feed stream and the side cooler duty (top section) for different locations of the side cooler (top section). The highest rates of meth-

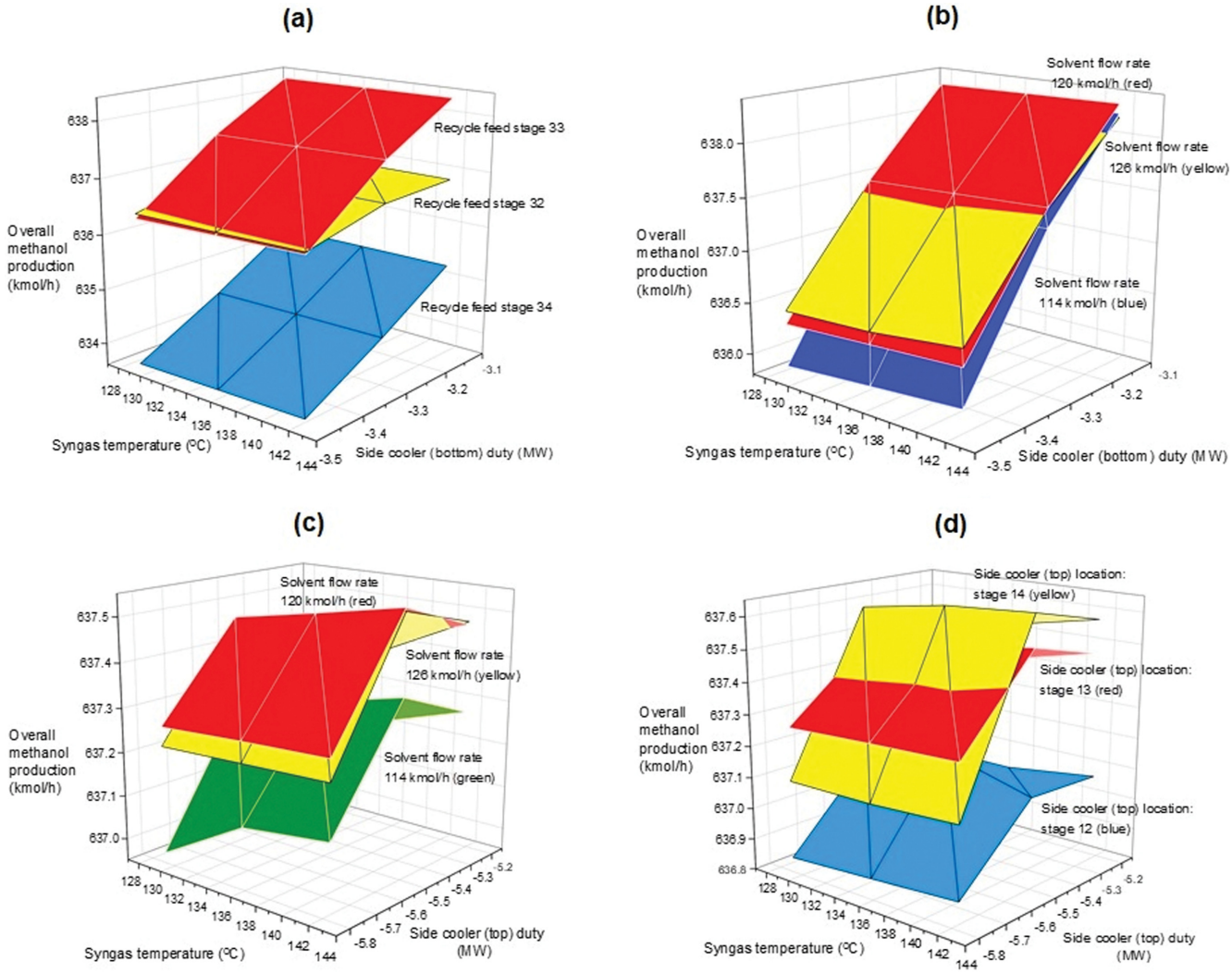

Fig. S3. Multi-parameter sensitivity analysis results for Case-I.

anol synthesis are obtained for stage 14, even though the design algorithm determines 13 as an optimal location for the side cooler. However, the difference between the optimum rates of methanol production obtained by the design algorithm and that shown in Fig. S3(d) is not significant (0.02%). The rates of methanol production obtained for stage 12 as the side cooler location are lower than the rates when the cooler is located on stage 13.

Therefore, it may be concluded that the rate of overall methanol production obtained by the design algorithm is optimal. Most of the points (combination of design variables) for which higher rates of methanol production (relative to the one obtained by the proposed design methodology) are observed are not valid as the constraint on the maximum allowable reactive stage temperature is violated at those points. Among the feasible points obtained by the sensitivity analysis, the maximum overall rate of methanol production differs from that obtained by the design algorithm by 0.3% only.

In addition to the multi-parameter sensitivity analysis, the NLP given by Eqs. (A1) to (A6) was also solved to obtain the maximum methanol production in the process, shown in Fig. 1. The exercise was performed for the syngas composition used in Case I using Sequential Quadratic Programming (SQP) for optimization.

$$\underset{T_{0,R},\, T_{0,G},\, T_{0,S},\, Q_i}{\text{Maximize}} \; F_{Methanol} \tag{A1}$$

subject to:

$$T_i \leq 270 \tag{A2}$$

with the following bounds on the variables:

$$a \leq T_{0,G} \leq b \tag{A3}$$

$$c \leq T_{0,S} \leq d \tag{A4}$$

$$e \leq T_{0,R} \leq f \tag{A5}$$

$$g \leq Q_i \leq 0 \tag{A6}$$

where, $F_{Methanol}$ is the total amount of methanol in the produced (in the "Crude methanol" stream of Fig. 1), Q_i is the heat duty of stage '*i*' ('i'=1, …., 44) (in MW), $T_{0,G}$, $T_{0,S}$ and $T_{0,R}$ are the feed temperatures (in °C) of syngas, solvent and recycle gas, respectively.

Since the aim is to compare results obtained with the proposed design methodology and the NLP problem, the solvent flow rate was kept the same as the optimum values given in Table 4. The two variables- recycle feed stage and cooler location (stage) are integers and not used in this problem. Rather, the NLP was solved for different recycle feed stages around the optimum stage (3 above and 3 below) shown in Table 4. Side coolers were allowed on all stages and as shown in Eq. (A6), the upper bound has been kept zero, i.e. the optimum solution can either have a cooler on any stage, or none. The bounds for the temperatures and lower bounds of the heat duties were varied as part of the exercise. Some of the observations for Case I_Alt, relative to the results Table 4 are as follows:

(i) When feed streams were allowed to attain higher temperatures than the values in Table 4, the methanol production obtained was ~1% higher. The per pass conversions of reactants were higher (by ~9% for CO) with higher heat removal (~76%) in the side coolers. However, since the optimizer had the option to use side coolers on all stages, 35 coolers were used (with non-zero heat duty), which is not practical. Another important fact was the requirement of higher temperatures in the recycle and solvent feed streams, which increases the energy requirements.

(ii) When the upper bounds of the temperatures of the feed streams were restricted to the optimum values (obtained by the design methodology), shown in Table 4, the temperatures of the feed streams were found to drop and touched the upper bound for the gas recycle stream. The overall methanol production was ~0.2% higher and the per pass CO con-

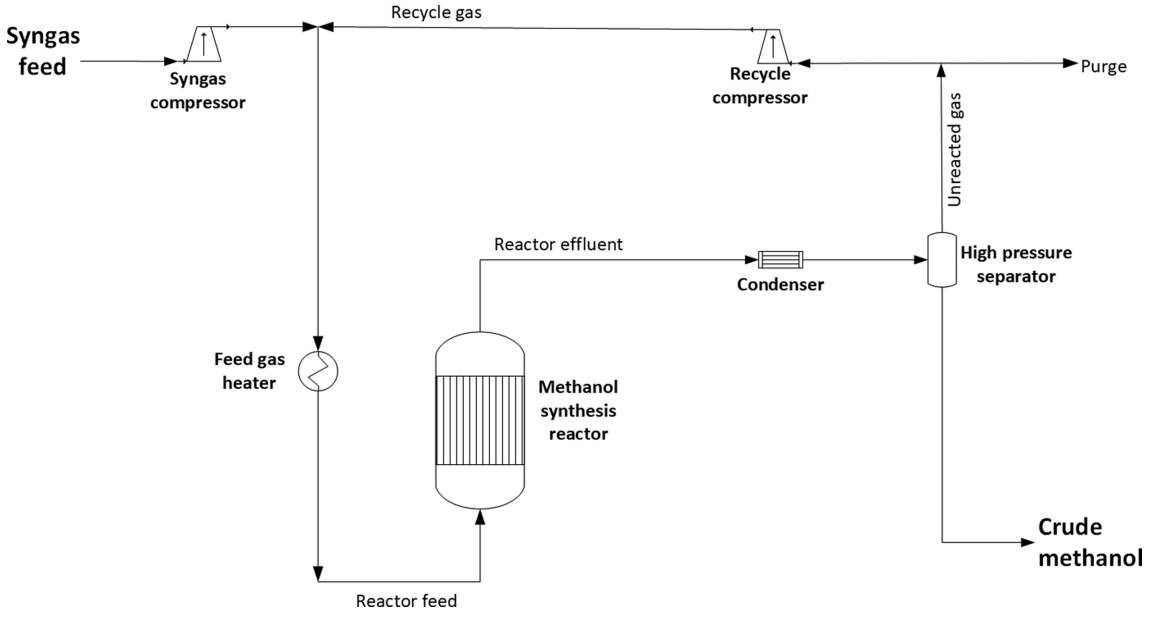

Fig. S4. Flowsheet of the simulated PBR-based process.

version was higher by ~3%. The number of side coolers now became 20 and the amount of heat removed is higher by ~8%. In this regard, it is important to note that another important criteria for optimality of the solution obtained by the design methodology is that the per pass conversions of the reactants must also be optimal along with the overall methanol production. This observation also demonstrates the optimality of the conversions of the design obtained with the proposed methodology. The optimal conversion obtained by solving the NLP is higher by ~3% (for CO) and this can be attributed to higher number of coolers (20 vis-à-vis 3 obtained with the proposed methodology).

(iii) When different initial guesses are used, the optimum methanol production was found to be within 0.06% with similar per pass conversions of reactants. This shows the possibility that the global optima may not be significantly higher than the local optimum, obtained as the solution.

These observations are in line with the conclusions made from the multi-parameter sensitivity analysis, described in this section and therefore, suggest that a local optimum can be reached by using the design algorithm.

S4. Flowsheet of 2 Phase Process

The flowsheet of the PBR-based process simulated in this work is given in Fig. S4.