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Dimian, Alexandre C.; Kiss, Anton A.

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# Enhancing separation efficiency in the acetic acid manufacturing by methanol carbonylation

Alexandre C. Dimian,<sup>1</sup> Anton A. Kiss<sup>2</sup>

<sup>1</sup> University "Politehnica" of Bucharest, Polizu 1-7, 011061 Bucharest, Romania

<sup>2</sup> Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, 2629 HZ, Delft, The Netherlands

## Keywords

Acetic acid manufacturing; Chemical process design; Process simulation; Sustainable chemical process; Energy efficiency

## Abstract

Acetic acid is an essential chemical used in the production of many chemical products. Using methanol as bio-building block, the acetic acid produced may be incorporated in bio-based products. This study deals with enhancing the efficiency of separations in a process using homogeneous catalyst, which is the most applied today industrially. Several configurations for downstream processing by distillation are investigated using effective combinations of fully thermally coupled columns, namely dividing-wall columns, alone or combined with heat pumps.

The results show that the three-column direct sequence may be effectively replaced by a two-column sequence. When only full thermally coupled columns are employed, the alternative C1+DWC(C2+C3) performs the best with savings of 25% in CAPEX, 27% in OPEX and 24.5% in CO<sub>2</sub> emissions. When vapor compression is added (using water as working fluid), the alternative DWC(C1+C2)+C3-HP performs the best. CAPEX remains at 10% under the base-case, while the savings in utilities and CO<sub>2</sub> emissions rise to 46.8% and 53.3%, respectively. Overall, the total annual cost is reduced by 34%. The cost of compressor may be paid back in 1.5 years by the saved energy. Low energy intensity (under 1 MJ/kg acetic acid) is achieved by tight integration with the reaction section.

## 1. Introduction

In the pursuit for a more sustainable future, the chemical process industry is making major changes to improve the energy efficiency and to reduce its carbon footprint, while at the same time remaining competitive and cost-effective in producing a range of essential chemicals. This trend poses new challenges and opportunities for the design of innovative processes based on renewable raw materials.[1] In this context, methanol is a key bio-building block that allows the recovery of every source of waste carbon as syngas. Furthermore, methanol can be used in a wide range of applications, as for example producing olefins (ethylene and propylene) today mostly based on petrochemical sources.[2] Amidst stricter regulations and growing environmental awareness around the world, there is an impending shift of acetic acid production strategy in favor of greener processes.[3]

Acetic acid is an essential chemical intermediate used in the manufacture of many consumer products, as vinyl acetate (about 33%), acetic anhydride and ester production, as well as various polymers, coatings, paints, and solvents.[4,5] Combining both green acetic acid and ethylene sourced from methanol results in manufacturing sustainable vinyl-acetate monomer (VAM), the main acetic acid consumer today, by using an energy efficient process.[6]

The global production of acetic acid was 9.1 million tons in 2019, with the perspective of a sustained increase in the next years.[7] The largest producers of virgin acetic acid are Celanese and BP Chemicals. Acetic acid is produced nowadays at industrial scale both synthetically and by bacterial fermentation. The main manufacturing route is based on the methanol carbonylation, with a market share of about 75%, [4] using either homogeneous or heterogeneous catalyst. Despite the efforts, the bio-based process routes based on fermentation [8] is still limited to only 10% of the market, due to poor economics in the separation and purification steps, [9] but it still remains important for the production of vinegar in the food industry. Other processes to produce acetic acid include methyl formate isomerization, conversion of syngas (bio-based or fossil) to acetic acid, and gas phase oxidation of ethylene and (bio)ethanol. [4,5]

The advances in the acetic acid processes and catalysts aim primarily to reduce the raw material consumption, energy requirements, and the investment costs. [10,11] The efforts to improve the catalyst performance resulted in the rhodium catalyst (Monsanto process) and iridium-base catalyst (Cativa™ process) as homogeneous catalysts that operate with high activity at reduced water concentration. [12-14] The Cativa process is greener and more efficient, and for these reasons, it has largely replaced the Monsanto process. A leap forward was achieved by the development of heterogeneous catalysts. [10,11] However, in all industrial processes it is vital to reduce the energy intensity of the fluid separations. [15]

A recent study has developed the conceptual design of a novel eco-efficient process for acetic acid manufacturing by methanol carbonylation using heterogeneous catalysis. [16] The sustainability indices showed significant improvement with respect to a classical homogeneous process. However, the homogeneous catalyst concerns today about 85% of methanol carbonylation processes.

Therefore, it is challenging and important to explore the possibility of enhancing the homogeneous catalyst process by applying process intensification methods, such as fully thermally coupled distillation (either dividing-wall column or Petlyuk systems) and heat pumping. More specifically, the goal of this original research study is bringing energetic intensity of a homogeneous process below 1 MJ/kg. The design regards a plant producing 25,000 kg/h (200 ktpy) acetic acid of standard purity of 99.5%. The analysis and design is performed by employing the rigorous process simulator Aspen Plus v11.0.

## 2. Process simulation approach

The base-case design follows the classical processes as developed by Monsanto [4] and Cativa [12] and simulated in our previous work. [16] This is briefly reviewed in the next section. The simulation emphasizes the strong dependence of the energetic costs as function of purity, namely at higher values. For this reason, in the first step the target for evaluation of alternatives is the standard industrial value of 99.5%. [4] Dividing-wall column (DWC) can be considered as a single shell realization of fully thermally coupled columns, such as the Petlyuk arrangement. The design and simulation of such devices is well established at industrial scale. [17,18] The present work includes the following steps:

- Building-up a base-case design for a state-of-the-art process based on homogeneous catalyst.
- Development of new designs employing dividing-wall column (DWC) and heat pumping.
- Process comparison in terms of key performance parameters (economics and sustainability metrics).

The evaluation of alternatives is performed by sensitivity analysis by rating the overall performance by means of the total annual cost (TAC), according to a general accepted industrial practice. TAC includes fixed capital (purchasing and installation) costs, as well as utility costs.

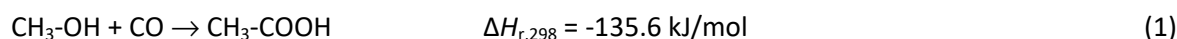
### 3. Base-case design and simulation

Figure 1 presents the base-case flowsheet comprising the reaction and separation sections.[16] The production capacity is 25,000 kg/h acetic acid (416.3 kmol/h). The yield estimates are 98 % for methanol and 95% for CO.[4] The plant inputs are methanol (424.8 kmol/h = 13,612 kg/h) and CO (438.2 kmol/h = 12,274 kg/h), according to the preliminary material balance.

Note that the base-case is the same as in our previous work,[16] since the goal is comparing the two processes (homogeneous and heterogeneous catalyst) for the same chemical reactor performance. However, the sharing of recovered heat duties in the recycle is slightly modified: steam generator from 6.19 to 5.55 MW and heat exchanger H-4 from 6.24 to 7.0 MW (in total 12.43 vs. 12.44 MW). This change corresponds to the optimal results from the previous paper from the integration of reaction and separation section (see original Fig. 4).[16] Namely, the outlet temperature from ST-GEN is 160 °C, which ensures a larger driving force for LP steam generation, while the heat duty of 5.5 MW becomes a constraint for heat integration. A larger duty of H-4 is exploited for additional power generation by ORC.

#### 3.1 Reaction section

The methanol carbonylation is described by the following overall stoichiometric equation:



The moderately exothermic reaction takes place in liquid phase at 180-250 °C and 30-40 bar. The catalyst is a rhodium complex in the Monsanto process[4] and a complex based on iridium in the Cativa process,[12] involving methyl iodide (CH<sub>3</sub>I) and hydrogen iodide (HI). Methyl acetate is used as a solvent. The catalytic complex is maintained by recycling CH<sub>3</sub>I, HI and a controlled amount of H<sub>2</sub>O.

The chemistry is complex when examining the catalytic reaction mechanism. This aspect has profound implications on conceptual process design.[12,16] The reaction rate is essentially first order in both catalyst concentration and methyl iodide concentrations, but independent of the reactants' concentrations. Therefore, high conversions can be obtained even in a continuous stirred-tank reactor of relatively small volume.[19]

The use of iridium as coordinating metal is justified by a much lower price but it has also a significant impact on reactor productivity. The reaction rate may increase considerably by using "promoters", which may be iodide complexes of zinc, cadmium, mercury, gallium and indium, as well as carbonyl-iodide complexes of tungsten, rhenium, ruthenium and osmium.

Although the methanol carbonylation is highly selective, some secondary reactions may be noted. The water gas shift reaction leads to CO<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub>. Acetaldehyde with hydrogen gives ethanol, and further propionic acid by carbonylation, which is the main heavy impurity.

The chemistry and kinetics are complex matters, but the fast reaction achieves practically total conversion with excellent yield. In the workable regime, the reaction rate can be mastered mainly by the catalyst amount, including co-catalyst and promoters, since the reaction is zero-order with respect to the concentration of CO and methanol. Thus, a first design issue is recycling all the components of the catalyst recipe that are carried out with the outlet reaction mixture to the separation section.

#### 3.2 Separation section

The separation section is fed by the stream PROCESS that leaves FL-3 as vapour at 1.5 bar and 125 °C. The mass composition (kg/h) is: acetic acid (25,662), methyl acetate (2,296), CH<sub>3</sub>I (1,999), propionic acid (148), MeOH (4), CO (235), CO<sub>2</sub> (78), CH<sub>4</sub> (22). Vapor pressure is the key property for determining the separation sequence. Methyl iodide is the most volatile (nbp 42.4 °C), followed by methyl acetate (56.9 °C), methanol (64.7 °C), water (100 °C), acetic acid (117.9 °C) and propionic acid (141.2°C).

As shown in Figure 1, a *direct sequence* of three distillation columns is appropriate and typical for the homogeneous process.[4,5] The direct sequence separation is justified by the nature of components and mixture's composition: significant amount of lights, majority acetic acid (as final product), and reduced amounts of heavies. The first column C-1 removes the lights as top distillate (vapor and liquid), while the bottom recovers completely the entrained rhodium catalyst as acetic acid solution. Note that catalyst recycling with negligible loss of expensive rhodium is a hard technology constraint. This is the reason of heterogeneous CT-ACETICA process (Chiyoda) in which Rhodium is fixed on a polymer resin. The volatility of the Rh imbedded complex is virtually impossible to evaluate fully. It should be observed that the chemical structure involves highly volatile species (such as HI, CH<sub>3</sub>I and methyl acetate). By depressurization from 35 to 1.6 bar there is very likely that some Rh (even in tiny small amounts) may be entrained in the vapor phase. The role of first distillation column is to remove and recycle the lights, as well as securing the full recovery of Rhodium catalyst.

A concentrated acetic acid mixture is taken over as vapor side-stream and sent to the column C-2. Here the acetic acid dehydration takes place, the distillate recovering completely water and lights. The vapor distillate from C-1 and C-2 enters column C-4 where the lights are recovered by absorption in methanol. A final cooling at 5 °C removes the entrained methanol from the vent gases. The condensate and top distillates are recycled to the chemical reactor. In this way, the catalyst composition is preserved. However, a makeup of methyl iodide might be necessary to compensate losses in exit gaseous streams. The water inventory should also be balanced. The bottom stream of C-2 is sent to the column C-3 where high purity acetic acid is obtained as top product.

The separation sequence was simulated in Aspen Plus v11.0 using the VLE property model NRTL-Hayden-O'Connell (NRTL-HOC) with Henry components. The validation of various VLE models against experimental data is provided in the *Supplementary Material*.

As column internals, we use structured packing. This allows significantly dropping the tower size, both in terms of diameter and height. The best results were given by Mellapak Plus 252Y from Sulzer.[20] This may ensure a HETP of 0.33-0.42 m over a flow parameter range of 0.5 to 4. We consider in design a conservative HETP value of 0.5 m. Remarkably, the pressure drop may be reduced bellow 20 mbar/m. The column pressure drop may be maintained bellow 0.1 bar, resulting in lower bottom temperatures and cost-effective reboilers, which typically may represent 40-60% of the cost of a distillation column.

The main operation parameters and the sizing of internals are provided in the *Supplementary Material*. Column C-1 has 17 theoretical stages, the vapor inlet entering close to reboiler. The diameter is varied in three steps, 1.0/1.2/1.75 m, to accommodate large variations in vapor and liquid flows but keeping the hydraulic regime at 70-80% from flooding.

The removal of water in C-2 is difficult since the equilibrium curve shows a tendency to azeotrope formation. The column needs 35 theoretical stages, the vapor feed being located above the stage 27. Changing the tower diameter is necessary, this time larger in the middle, as 1.3 m in the range of stages 2-15, 1.75 m for stages 16-26 and 1.9 m for stages 27-34. Dividing the column in three regions corresponds to different separation requirements. The water removal increases continuously from bottom to the top, while the opposite happens for the acetic acid. In the middle section above the feed the vapor flowrate increases suddenly, and thus need a larger cross section is necessary.

Finally, acetic acid is obtained as top product of column C-3 with a purity of 99.5%. The bottom stream contains heavies, such as propionic acid. Column C-3 is provided with 35 trays. The separation is tedious, as the K-value of acetic to propionic acid is around 1.20. Accordingly, the separation needs higher reflux flowrate. The total hot utility duty is  $2.5+4.5+4.5 = 11.5$  MW.

### 3.3 Influence of purity on the energetic requirements

The energetic requirements of the separation section namely depend strongly on the acetic acid purity. Figure 2 shows the relative increase in total hot utility consumption in the base case on the interval 99.5 to 99.9%. The rise is limited to 10% at 99.65%, but it escalates above 60% if 99.9% purity is required. As consequence, the comparison of alternatives will be done on achieving the standard acetic acid purity of 99.5%, but this aspect will be reconsidered at the final selection.

## 4. Thermally coupled distillation configurations

### 4.1 Configuration DWC(C1+C2) + C3

As illustrated in Figure 3, the columns C-1 and C-2 are combined into a single dividing-wall column DWC(C1+C2). Stream PROCESS enters the left side (C1 region), where the pre-separation supplies top vapor and bottom liquid streams to the C2 region. C1 has 8 theoretical stages, the vapor feed stream entering the bottom stage. C1 also receives liquid and vapor streams resulting by splitting reflux and boilup streams issued from the region C2. As in the base case, section C2 has 35 theoretical stages. The number of stages results from the optimal integration of columns C-1 and C-2 with the reaction section as described in a previous paper,[16] which is kept here for a fair and consistent comparison of designs. The split of reflux and boilup flows takes place in C2 at the level of stages 17 and 26, respectively. The inter-zones mass flows are set at 5,000 kg/h. In C1 the reflux ensures the concentration of heavier species in the bottom flow, while the lights and water rise to the top joining the vapor flow in C2. In this way the top distillate from DWC(C1+C2) removes at the top the lights and most of the water, while the raw acetic is taken over as liquid side-stream from stage 30. The final purification takes place in C-3 (35 stages) which delivers purified acetic acid as top product and heavies in bottoms. In this way, a three-column sequence reduces to only two columns. There is a capital cost reduction, whose benefit depends on the cost of the scrapped equipment. Looking at the cost of individual items it seems that condenser, reboiler and auxiliary equipment may value much more than tower and internals. For this reason, the reconfiguration of distillation sequences by DWCs is particularly beneficial in revamping projects.

The simulation flowsheet and key results are displayed in the *Supplementary Material*. The target is getting acetic acid purity of 99.5%. Table 1 presents material balance, operating parameters, and sizing characteristics. The DWC is operated with partial condenser such to remove all lights. Top pressure of 1.1 bar and column pressure drop of 0.1 bar result in the temperatures in condenser and reboiler of 52.2 °C and 124.2 °C, while the side stream is at 123.1 °C. Employing Mellapak Plus 252Y (with HETP of 0.5 m) results in packing zones of 4 and 16.5 m for DWC, and 16.5 m for C-3. The hydraulic calculations were done by applying an efficient interactive tool in Aspen Plus for internals sizing. The graphical presentation of results allows modifying the type of internals and geometrical characteristics such as to get the adequate behavior. Hence, pressure drops of about 0.05 bar in DWC (C1+C2) and 0.032 bar in C-3 are obtained, well below the assumed value of 0.1 bar. The hydraulic sizing including the equilibration of pressure drop must on each side is handled in a later section. The temperature difference in reboilers is at least of 20 °C with respect to LP steam at 150 °C. Table 1 also presents the equivalent diameters of zones resulting from computer simulation. The sizing of the column C-3 is similar to the base case. The duties of reboilers are 5.0 and 4 MW (9.0 MW in total).

### 4.2 Configuration C1 + DWC(C2+C3)

This option combines the columns C-2 and C-3 in a DWC (C2+C3), as depicted in Figure 4. Column C-1 removes most of the lights and water in top and return in bottoms the entrained catalyst, while the raw acetic acid obtained as vapor side stream enters the DWC. In DWC, the purified acetic acid is extracted as liquid side stream, while the water and heavies are removed in top and bottoms, respectively.

Column C-1 has 17 stages and DWC(C2+C3) 10 and 35 stages. The temperatures in top, side stream and bottoms in C-1 are 35, 117.7 and 122.9 °C, and in DWC 46.9, 122.9 and 128.2 °C. For column (C-1) suitable hydrodynamics is fulfilled with packing divided in three segments of 1.1, 1.2 and 1.7 m. In the DWC unit the C2 zone has a diameter of 1.4 m, except the vapor feed zone where simple Pall rings are more suitable. Zone C3 is divided in three sections corresponding to the vapor flow traffic, which results in an enlarged middle section of 2.4 m and top and bottom parts of 2.1 m. The pressure drop is kept in all units below 0.05 bar.

#### 4.3 Configuration Petlyuk(C1+C2) + C3

In this configuration the first two columns are fully thermally coupled but as separate shells (Figure 5). The simulation shows that the pre-fractionator (C-1) may be reduced to only few stages. Only the liquid back stream from C-2 is necessary as reflux in C-1, while the vapor back-stream may be skipped.

As demonstrated earlier,[21] such setup that is appropriate for handling mixtures containing relatively small to moderate light amounts (including highly volatile and supercritical species) but few heavies, as well as a majority of intermediate components. Moreover, when reduced to a flash coupled to a distillation column this device (called "flash-compact distillation") may be applied as an effective first-separation step.[22] Typical applications are the separation of mixtures issued from the oxidation of hydrocarbons, as by phthalic anhydride from paraxylene, maleic anhydride from butane, as well as in some hydrogenation reactions, as liquid-phase hydrogenolysis of fatty esters to fatty alcohols.[23] The simulation shows that the Petlyuk configuration has similar sizing characteristics and performance as C1+DWC(C2+C3), but the advantage of a simpler mechanical construction and lower equipment cost.

In the Petlyuk configuration, vessel C-1 has 3 stages with feed in the middle and reflux from C-2 on top. The column C-2 has 35 stages with vapor feed and liquid feeds on stage 18 and 26, respectively, while a side-stream from the stage 27 (5,000 kg/h) is sent back to C-1. Since the vapor flow is larger over the stage range 9 to 17 the diameter is enlarged to 2.2 m, while for the other stages this is kept at 1.85 m, the operation between placed at about 80% from flooding. The column C-3 has 35 stages and a diameter of 1.6 m.

### 5. Heat pump assisted thermally coupled distillation

The performance of thermally coupled distillation configurations analyzed before can be further improved by using heat pumps.[24] The approach is favored by the low temperature difference between the hot and cold sources, as well as by the possibility of using water as working fluid. Since water is used as a thermal agent, the effect may be cumulated with the on-site steam, either on the same reboiler, or as separate side-stream exchanger. The compression ratio (CR) may be determined from the ratio of outlet / inlet compressor pressures (which is shown in all related figures), and it is about 4.5 in three compression stages with intermediate cooling except for the last stage.

The compressor purchasing cost has been calculated with relation:  $C = 580,000 + 2000 \times [W, \text{kW}]^{0.6}$ . [25] By assuming an installation factor of 1.5 results in the total cost  $C_{cp} = 1.5C$ . In the subsequent cases an installed power of 700 kW was found suitable, which gives a total compressor cost of 1.7 M\$. The heat exchange replaced units, condenser and reboiler, have been sized and estimated as cost by the Economic Analyzer from Aspen Plus v11.0. The equipment was completed with the additional items (such as condensate accumulator, reflux pump) from the corresponding DWC only alternatives, in order to get consistent cost estimation. The cost estimation in Aspen Plus also takes into account different sections generated by diameter variation.

#### 5.1 Configuration DWC(C1+C2) + C3&HP

This option enhances the DWC setup examined before by adding a vapor compression heat pump on the

final purification step. As presented in Figure 6, the top vapor from C-3 at 1.1 bar and 120.7 °C enters the hot side of the condenser H-1 in counter-current with the thermal agent, boiling feed water, at 1.2 bar and 104.8 °C. The resulting steam is compressed to 4.6 bar by the compressor CP-1, three stages with intermediate cooling except the last one that supplies superheated steam slightly below 200 °C. The superheated steam enters the unit H-3 that plays the role of reboiler. The stream obtained as bottoms minus the heavy product is vaporized and sent as boilup to column C-3. The condensed water is depressurized to 1.2 bar and cooled in valve V-1, thus restoring the cycle. The heater H-2 may provide supplementary cooling for conditioning the reflux stream. Supplementary duty (unit H-4) is injected as side-heater for completing the heat necessary to achieve the desired purity and for start-up purpose.

The implementation of a heat pump on the top vapor stream does not affect the L/V traffic and thus preserves the separation process. In this case the duty of the condenser H-1 of 3.3 MW is lifted to 3.6 MW in the reboiler H-3, by adding a net energy of 0.3 MW injected by vapor compression. This results by subtracting from the compressor power (674 kW) the losses by inter-stage cooling (300 kW) and by considering a mechanical efficiency of 0.92 (an isentropic efficiency of 0.72 was used in calculating the compressing power). For achieving 99.5 % purity a small duty of 0.3 MW should be injected on stage 35. The net hot energy used is therefore  $3.7+0.3 = 4.0$  MW, as with the DWC only alternative (Table 1).

The heat pump is driven by 5,800 kg/h water and has a COP of  $3.6/0.674 = 5.34$ . The net hot utility consumption is  $5.0+0.3 = 5.3$  MW which compared with 9.0 MW (Table 1) indicates savings of 41%.

## 5.2 Configuration C1+DWC(C2+C3&HP)

This option, similar to the one shown in Figure 4, considers adding a heat pump on the side-stream product of the DWC column (as depicted in Figure 7). This stream enters the condenser (H-1) while water is evaporated on the other side. The vapor is compressed to 4.6 bar and 194 °C in a three-stage compressor (CP-1) for driving the heat exchanger H-2 playing the role of reboiler in countercurrent with the bottom stream of the column C-3. After full condensation and decompression through valve V-1, the resulting liquid water stream closes the cycle. The heat pump is driven by 5,300 kg/h water and works between 101 °C (1.05 bar) and 148 °C (4.5 bar). The three-stage compressor with intermediate cooling supplies from the last stage superheated vapor at 4.5 bar and 198 °C, which is below 200 °C the recommended upper limit.[26] Following the same reasoning as before, it results that the compression power (622 kW) is used for lifting the duty of condenser H-1 (3.0 MW) as duty of reboiler H-2 (3.3 MW), by adding 0.3 MW as well. In addition, to achieve 99.5 % purity, 4.0 MW should be added in an additional steam reboiler. The total hot energy is  $2.5+4.0 = 6.5$  MW, which compared with the 8.5 MW of DWC only arrangements gives savings of 23.5%. The COP of the heat pump is  $3.3/0.62 = 5.30$ .

However, the simulation shows that raising from 35 to 40 the number of stages in the C3 zone is necessary to achieve the purity specification. The vapor product is drawn from the stage 32. The top pressure in C-1 is 1.25 bar, while in DWC(C2+C3) 1.15 bar. The side-stream leaves at 124.4 °C, while the top and bottoms temperatures are at 105.2 °C and 126.9 °C. The temperature difference is 23 °C in condenser and 21 °C in reboiler.

## 6. Comparison of process alternatives

Table 2 and Table 3 present the key performance indicators for the thermally coupled arrangements vs. base-case, the target being a product purity of 99.5%. Fixed Capital (FC) cost includes Purchasing Cost of Equipment and Installation costs. Utilities (Ut) account for cold utility (cooling water), hot utility (LP steam) and electricity. The capital and operation elements can be captured in a single parameter, the Total Annual Cost, calculated following the relation  $TAC=FC/3+Ut$ . The CO<sub>2</sub> emissions correspond to hot utilities only. The results have been retrieved from the Economic Analysis and Energy Analysis tools available in Aspen Plus v. 11.0. Details can be found in the *Supplementary Material*.



Table 2 lists the performance of DWC alternatives. The configuration C1+DWC(C2+C3) achieves the best saving in terms of fixed capital, utilities, TAC and CO<sub>2</sub> emissions, namely 25.0, 27.9, 27.0 and 24.5%, respectively, as compared with DWC(C1+C2)+C3, where these are 15.2, 24.7, 21.7 and 20.0%. The difference between the two configurations may be explained in the cost of the scrapped equipment (reboiler and condenser heat exchangers, vessels and pumps), which is more expensive for unit C-2, as well as by the saved energy. The Petlyuk arrangement shows similar savings with the (C1+C2)+C3 arrangement, although with a notable advantage that it does not require DWC technology.

In the case of the thermally coupled arrangements including heat-pumps (Table 3), the configuration C1+DWC(C2+C3&HP) gives the best results. For compressor we consider an installed power of 700 kW that may cover largely the required power. The compressor cost is calculated with the relation  $C_{cp} = 580,000 + 2000 \times W[\text{kW}]^{0.6}$ . [25] This gives 0.682 M\$ purchasing cost, 1.023 M\$ installation cost (factor 1.5) and 1.705 M\$ fixed capital. The costs of the heat exchangers for replacing the condenser and reboiler are evaluated by Aspen Plus. Details are given in *Supplementary Material*.

Compared with the base-case the fixed capital saving is at 6.4%, but versus the corresponding DWC configuration it is 10.3% higher. However, the advantage is significant in saving of utilities and GHG emissions by 46.8%, and 29.4 %, respectively. The TAC is the lowest, at 5.2 M\$. The reduction in utilities and CO<sub>2</sub> emissions makes the difference with respect to the alternative C1+(C2+C3) examined before. The alternative C1+(C2+C3&HP) succeed to achieve saving in utilities and GHG, but the performance in term of costs is below the DWC counterpart.

In conclusion, the above evaluation demonstrates that the configuration (C1+C2)+C3&HP gives the best performance in term of reduction in total annual costs and energy saving. The second best is the alternative C1+DWC(C2+C3) which shows a good performance as well. However, when heat pumping is considered the alternative C1+DWC(C2+C3&HP) has disappointing results as this operation affects the separation process in the DWC column. Firstly, the lifted condenser duty is lower because it considers only the heat of product condensation, while in the other case this includes the reflux too. Secondly, the vapor draw-off flow diminishes the internal reflux flow, which can be restored only by more duty in the reboiler. Thus, the advantage of heat pumping is practically lost. The simulation reveals that the Petlyuk configuration is also suitable when applying conventional distillation technology.

A shortcut calculation may demonstrate the economic advantage. Considering a steam price of 15 \$/GJ the cost of thermal energy replaced in reboiler is  $3.7 \times 15 \times 3,600 \times 8,000 / 1 \times 10^9 = 1.60$  M\$/year. With an electricity price of 0.1 \$/kWh, the cost of compression is  $600 \times 0.1 \times 8,000 / 1 \times 10^6 = 0.48$  M\$. The saving is  $1.60 - 0.48 = 1.12$  M\$/year and thus the payback time of compressor  $1.70 / 1.12 = 1.52$  years.

## 7. DWC hydraulic design

The layout of internals in a DWC device must fulfill the requirements of proper coupling of the separation zones and the balance of the respective pressure drops.[17,27] The hydraulic calculations have been performed by using the interactive tools available in Aspen Plus for several internals, both trays and packings, aided by graphical representations. In this way, we determined that the most convenient packing is Mellapak Plus 512 Y from Sulzer. Table 1 presented the individual internals layout of the separated columns. The DWC layout is then combined by aligning the height of the common zones along the dividing-wall.

As example, we present the hydraulic design of the DWC(C2+C3), which was the best performant among the DWC alternatives. Figure 8 presents the liquid concentration profile of the ternary mixture acetic acid / water/ propionic acid together with several light species, along the 35 stages of the main column. The lights separate easy at top with water, whose concentration however needs about 17 stages to drop below 1 %wt. Then the separation enters the divided wall C3 zone that contains 10 stages, from 18 to 27. This is coupled with the pre-fractionator C2, which supplies vapor and liquid as feed streams at top

and the bottom, respectively. The concentration profile of the acetic acid is boosted in the wall zone, the purity of 99.5 %wt being approached asymptotically to the stages 25-27. The side-stream product is taken off on stage 27. Finally, the bottom zone 28 to 35 shows the separation of the acetic acid from heavies, here the propionic acid. The L/V traffic in the main column (see *Supplementary Material*) shows an interesting evolution. One notes maximum flows above the wall zone, just after the entry of a large vapor feed from C2 (stage 17), followed by decrease to the top. In the C3 wall zone the vapor flow shows a sudden drop, well below the liquid flow, but remaining almost constant down to the column's bottom. Regarding the liquid flow in the wall zone, this shows higher values than the vapor flow, but falls sharply after side-stream withdrawal. An important parameter in hydraulic design the reduced F factor  $F_{red}=Q_v \times \sqrt{\rho_v}$ , where  $Q_v$  is the vapor volumetric flow and  $\rho_v$  the vapor density. This profile suggests dividing the main column in four sections: wall zone, enlarged zone to accommodate the large L/V flows, as well as top and bottom zones. The rigorous calculation in Aspen Plus shows that this partition can be reduced to three sections: top, enlargement, wall plus bottom, with the diameters of 2, 2.3 and 2 m. The hydraulic plots show good flow patterns, with low pressure drop at flooding approach around 80%. A useful parameter in selecting structured packing column is the factor  $F_v = U_v \times \sqrt{\rho_v}$ , where  $U_v$  is the superficial vapor velocity (Sulzer, 2021). This can be obtained by dividing  $F_{red}$  by the cross-sectional area. Plots of HETP and pressure drop gradient versus  $F_v$  are supplied by commercial suppliers. Thus for Mellapak Plus 252 Y the plot shows HETP from 0.33 to 0.42 m for  $F_v$  from 0.5 to 3.5  $\text{Pa}^{0.5}$ . In this case the  $F_v$  varies in the range 2.0 to 3.0. The value HETP = 0.5 m is thus conservative.

The wall region is built by aligning the zone C2 and C3. Separately, these have the equivalent diameters  $d_1 = 1.3$  m and  $d_2 = 2$  m, and areas of 1.327 and 3.141  $\text{m}^2$ , respectively. The DWC diameter as given by the relation  $D = \sqrt{d_1^2 + d_2^2} = 2.385$  m. The wall position can be found from a relation regarding the area of segments formed by partition, given by  $A = (\theta - \sin(\theta))D^2/8$ ,  $\theta$  being the angle formed by the chord cut (radians). Thus, the distances to the column's shell for the zones C2 and C3 are 0.83 and 1.555 m, respectively, or in the ratio 0.35/0.65. The packing height that corresponds to 10 stages is 5 m.

The zones C2 and C3 should be also balanced as pressure drop. The zone C2 is built from 4 m Mellapak Plus packing and two Pall packing at bottom, better suited for a vapor feed (another alternative would using BX packing). The calculated pressure drop is 21.7 mbar. The zone C3 consists of 5 m Mellapak Plus packing, which results in a pressure drop of 11.7 mbar. The difference of 10 mbar may be compensated by providing a hydraulic resistance in the C3 zone path. The reflux and boilup partition between the two zones can be achieved by special devices available by specialized suppliers (e.g. Montz, Sulzer, Koch-Glitsch, Benit-M). By considering the other sections the total pressure drop is 50 mbar, well below the 100 mbar value assumed in simulations.

Finally the DWC column is built by assembling four sections: top (2.0x4.5); middle (2.3x3.5 m); DW (2.4x5 m); bottom (2.0x3.5 m).

The above discussion considers the frame of a new design. It is interesting to examine the application of DWC technology in a revamping project. From the three columns sequence only one unit can be reused in the DWC setup. This is C1 with DWC(C2+C3) or C3 with DWC(C1+C2). It remains that the column C-2 should be revamped as DWC unit. The solution depends on the internals previously employed. Typically, at the same L/V traffic the trayed columns shows larger diameters than structured packing columns. For example, an "old" C-2 column may be equipped with 33 sieve trays. The shell consists of two sections: top of 2.3 m diameter (25 stages) and bottom of 1.85 m diameter (8 stages). The comparison with the values given in Table 1 indicates that this column may be advantageously revamped as DWC(C1+C2) by employing structured packing. The database of internals in Aspen Plus 11.0 allows exploring several alternatives. The best results are obtained in this case with the structured packing Montz B1-250 MN, somewhat more compact than Mellapak Plus. The total packing pressure drop is about 70 mbar. Sizing details are given in the *Supplementary Material*. As a result, the configuration DWC(C1+C2)+C3&HP brings the best advantage in revamping as well.

## 8. Sustainability metrics

The previous design of the heterogeneous process achieved high eco-efficiency with respect to classical homogeneous process, such as low energy intensity of 0.78 MJ/kg product.[16] Here we examine the same issue after upgrading the design of the homogeneous process. As shown in Figure 1, the reaction section may generate 5.4 MW LP steam at 4.6 bar and 150 °C. On the other hand, 7 MW heat duty available on the interval 160-56 °C can be converted in electrical power by means of an Organic Ranking Cycle (ORC). By using iso-butane as thermo-fluid an efficiency of 0.194 may be attained,[16] and accordingly an electrical power of 1,358 kW generated.

Firstly, we examine the best alternative (C1+C2)+C3&HP. As thermal energy, the reaction section needs 1.33 MW for preheating, 1.45 MW to separate the product stream from the recycled catalyst in the unit FLASHER, so 2.78 MW in total. In the separation section, the reboiler duties are 5.0 in (C1+C2) and 0.3 MW in C-3, so 5.30 MW in total. By steam generation, 5.44 MW are available. It remains a net duty that need to be supplied of  $2.78+5.30-5.44 = 2.64$  MW. Regarding the electricity, the main consumers are CO compression (1,415 kW) and heat pumping (600 kW), in total 2,015 kW. Considering 150 kW for reactor mixing, pumping, and instrumentation, the total power consumption may be estimated as 2,165 kW. The electrical power needed from the grid then  $2,265 - 1,358 = 807$  kW. Considering an equivalence factor of 3 (electric to thermal), the above value corresponds to 2.42 MW thermal energy. The total energy duty resulting from simulation is then  $2.64 + 2.42 = 5.06$  MW that by assuming an uncertainty factor of 20% leads to a 6.07 MW. Since the production rate is  $25,000/3,600 = 6.94$  kg/s, the energy intensity is of  $6.74/6.94 = 0.875$  MJ/kg. This value is only slightly larger than the one found for the heterogeneous process (0.78 MJ/kg), but still below the target of 1 MJ/kg, which is remarkably low. The difference vs the heterogeneous process may be explained by the energy involved in the catalyst recycling, which needs an evaporation step and a supplementary distillation column. Implementing the DWC unit and heat pumping allows reducing the distillation sequence from three to two columns and getting substantial saving in energy, which results in the end in close performance of both processes.

## 9. Conclusions

This work successfully proved the feasibility of several innovative configurations for the downstream processing of acetic acid in the methanol carbonylation by homogeneous catalysis process. The results show that using thermal coupling (Petlyuk or dividing-wall column) instead of the conventional direct sequence allows important savings in capital, energy and GHGs. Among them, the best configuration is C1+DWC(C2+C3) that allows savings of 25% in fixed capital, 27% in utilities and 24.5% in CO<sub>2</sub> emissions. Total annual cost that captures both capital and operation costs is 6.16 M\$ (27% reduction). The alternative DWC(C1+C2)+C3 shows somewhat inferior performance, with savings of 22% in total annual cost, and utility and GHG savings of 25 and 20%, respectively. This alternative may be also implemented as a Petlyuk setup with the advantage of simpler construction.

When heat pumping is implemented as vapor compression (using water as working fluid) the alternative DWC(C1+C2)+C3&HP shows the best performance. The fixed cost increases (but remains 10% under the base-case), while the saving in utilities and CO<sub>2</sub> emissions raise significantly to 46.8% and 53.3%, respectively. Consequently, the total annual cost drops to 5.18 M\$. The investment in compressor and auxiliary equipment may be paid back in just 1.5 years. By tight integration with the reaction section, an overall energy intensity bellow 1 MJ/kg acetic acid is achieved. The recommended configurations can be applied in both new design and revamping projects.

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**Abbreviations**

COP	coefficient of performance	HOC	Hayden-O'Connell
CR	compression ratio	NRTL	non-random two-liquid
DWC	dividing-wall column	TAC	total annual cost
FC	fixed capital	TOC	total operating cost
GHG	greenhouse gas	VLE	vapor-liquid equilibrium

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## Tables

**Table 1.** Alternative designs involving heat integrated columns

Item	Unit	DWC(C1+C2)	C-3	C-1	DWC(C2+C3)
Feed	kg/h	32047	25300	32047	29800
Distillate V/L		1966/4588	25000	461/1432	920/3680
Side stream	kg/h	25300	None	29800 (v)	25000 (l)
Bottom		150	300	354	200
Stages/feeds *	-	8/8(v) 35/17(v)-25(l)	35/20	17/17(v)	10/10(v); 35/18(v)-28(l)
Side stream		30 (l)	None	14 (v)	27 (l)
Top pressure	bar	1.2	1.1	1.2	1.1
Pres. drop ass.	bar	0.1	0.1	0.1	0.1
Temp. Top	°C	54.7	120.5	35.0	48.0
Temp. SS	°C	126.9	None	117.7	123.0
Temp. Bottom	°C	124.1	127.2	124.2	124.7
Stages/diameter -/ m *		1-8/1.45 2-35/2.1	2-35/1.65	2-11/1.1/12-13/1.2/ 14-16/1.7	1-10/1.3 2-10/2.0 / 11-17/2.3 18-27/2.0/28-34/2.0
Total height	m	4.0: 16.5	16.5	7.5	5.0: 16.5
Pres. drop calc.		0.013/0.036	0.032	0.020	0.02/0.04
Condenser duty	MW	-9.28	-4.0	-2.94	-9.97
Reboiler duty	MW	5.0	4.0	2.5	6.0

\*Note: "Stages/feeds" refers to the number of stages in a section and the feed stages, while the "stages/diameter" refers to the number of stages and diameter of those stages in that particular column section.

**Table 2.** Performance of the thermally coupled (Petlyuk/DWC) arrangements vs. base-case

Description		Base Case	(C1+C2)+C3	Sav. %	C1+(C2+C3)	Sav. %	Pet(C1+C2)+C3	Sav. %
Equipment Cost	M\$	2.76	2.38	13.57	2.05	25.55	2.33	15.60
Installation Cost	M\$	4.60	3.86	16.14	3.46	24.75	3.83	16.70
Fixed Capital Cost	M\$	7.36	6.24	15.18	5.51	25.05	6.16	16.29
Total Utilities Cost	M\$/y	5.42	4.08	24.68	3.91	27.91	4.21	22.37
Total Annual Cost	M\$	7.87	6.16	21.72	5.75	27.02	6.26	20.47
CO2 emissions	kT/y	18.18	14.5	20.06	13.74	24.46	15.3	15.62

**Table 3.** Performance of DWC arrangements with heat-pumping vs. base-case

Description		(C1+C2)+ C3&HP	Saving to base case %	Saving to DWC %	C1+ (C2+C3&HP)	Saving to base case %	Saving to DWC %
Equipment Cost	M\$	2.46	10.78	-3.22	2.81	-1.75	-36.68
Installation Cost	M\$	4.43	3.78	-14.75	4.74	-2.99	-36.85
Fixed Capital Cost	M\$	6.89	6.40	-10.35	7.54	-2.52	-36.79
Utilities	M\$/y	2.88	46.84	29.41	3.50	35.49	10.51
Total Annual Cost	M\$	5.18	34.24	15.99	6.01	23.65	-4.62
CO2 emissions	kT/y	8.50	53.28	41.55	12.32	32.25	10.31

**Figure 1.** Flowsheet of acetic acid manufacturing by methanol carbonylation with homogeneous catalyst

**Figure 2.** Utilities consumption and CO<sub>2</sub> emissions as function of acetic acid purity, normalized to the base case (99.5%wt purity of acetic acid)

**Figure 3.** Alternative 1: DWC(C1+C2) + C3 flowsheet configuration

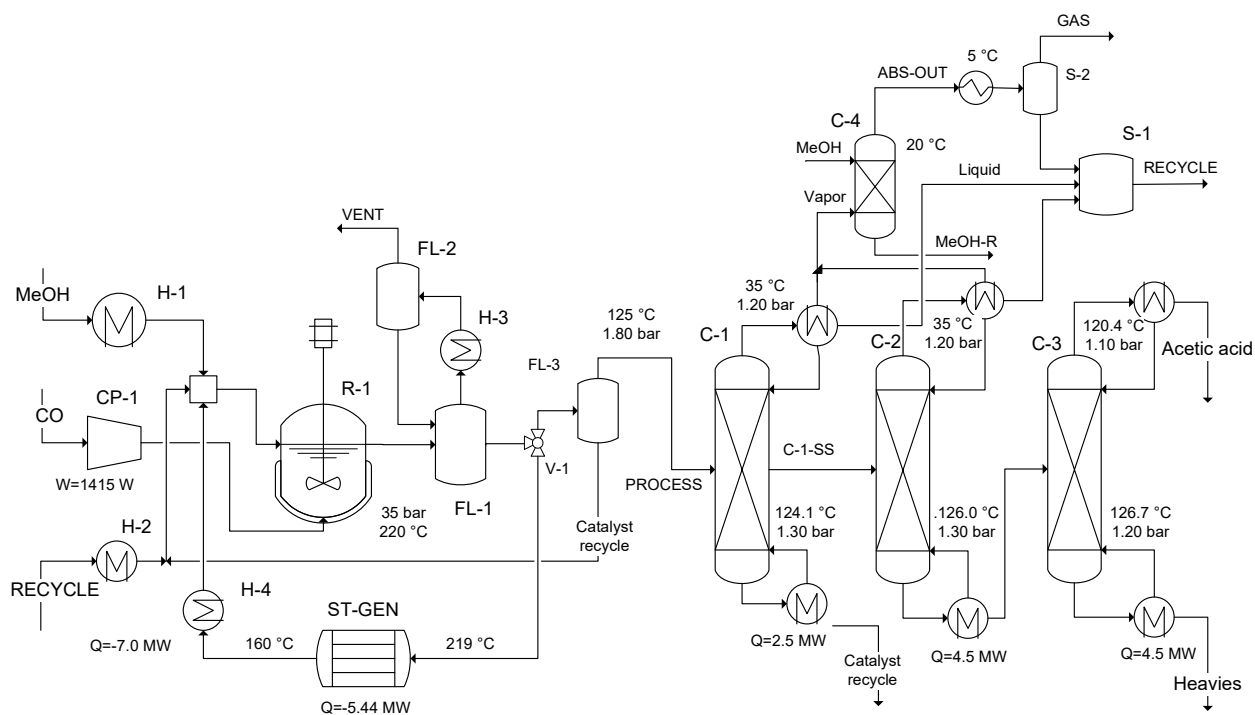
**Figure 4.** Alternative 2: C1 + DWC(C2+C3) flowsheet configuration

**Figure 5.** Alternative 3: Petlyuk set-up configuration (C1+C2)

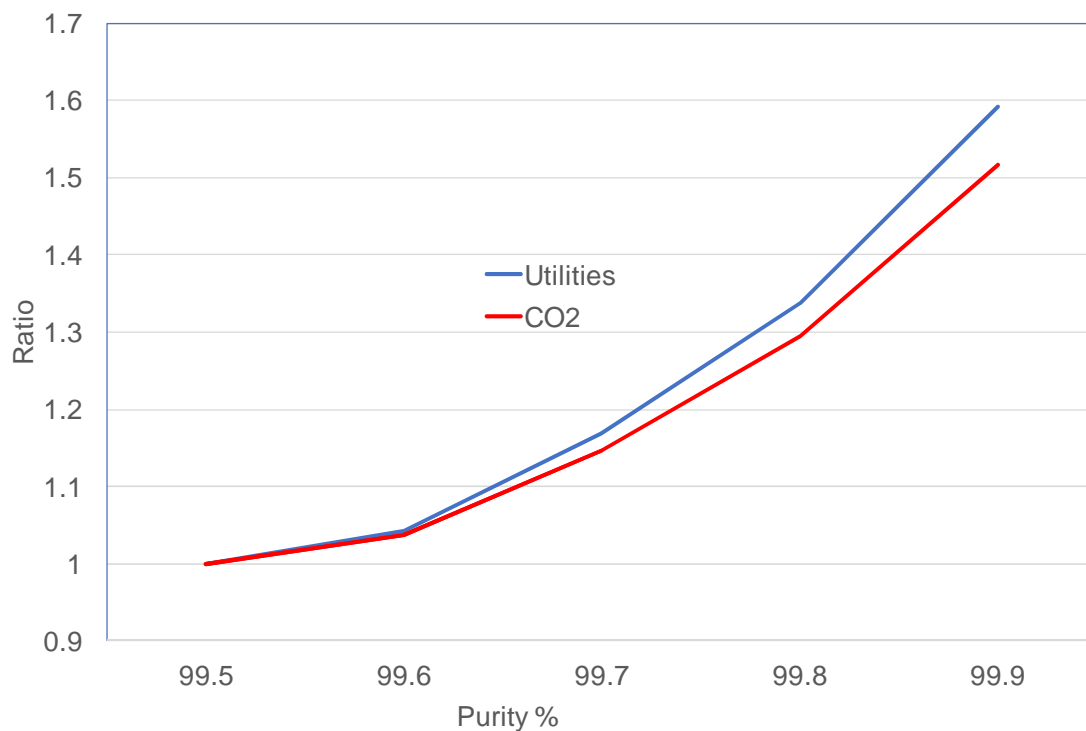
**Figure 6.** Alternative DWC(C1+C2) + C3 + Heat pump

**Figure 7.** Alternative C1 + DWC(C2+C3) + Heat pump

**Figure 8.** Liquid concentration profile in the DWC (C2+C3)



**Figure 1.** Flowsheet of acetic acid manufacturing by methanol carbonylation with homogeneous catalyst



**Figure 2.** Utilities consumption and CO<sub>2</sub> emissions as function of acetic acid purity, normalized to the base case (99.5%wt purity of acetic acid)



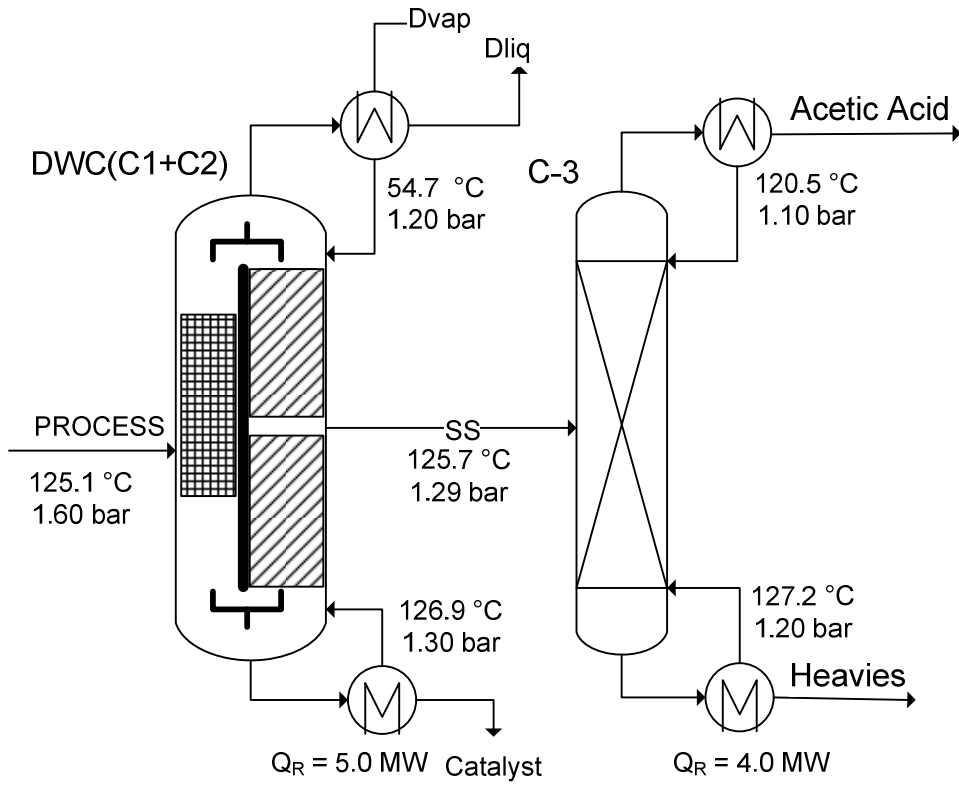


Figure 3. Alternative 1: DWC(C1+C2) + C3 flowsheet configuration

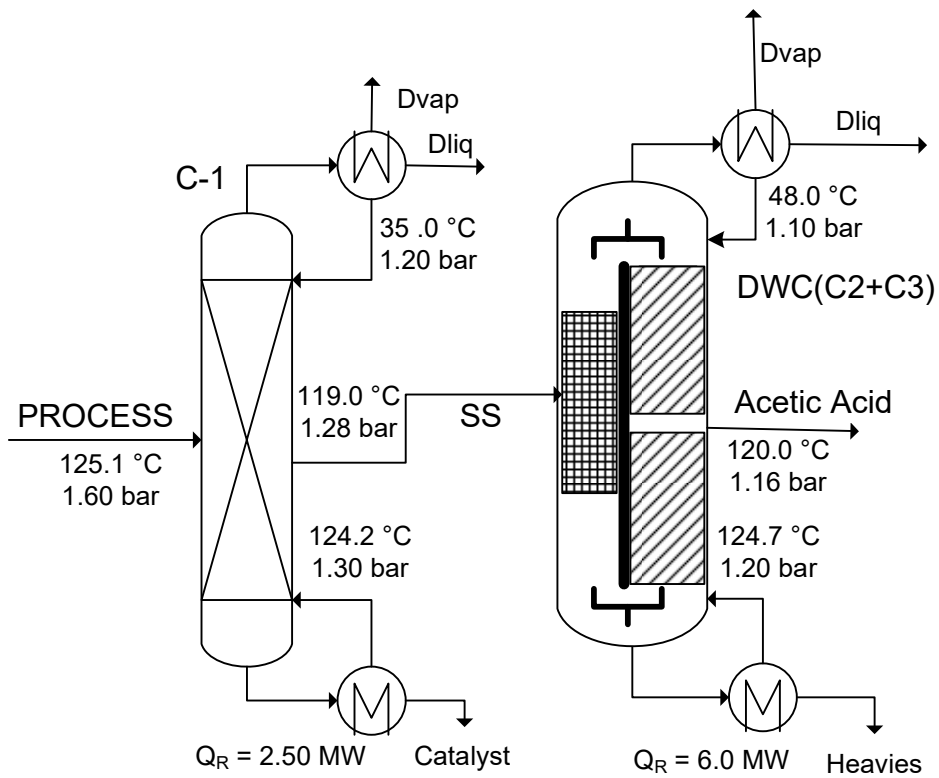


Figure 4. Alternative 2: C1 + DWC(C2+C3) flowsheet configuration

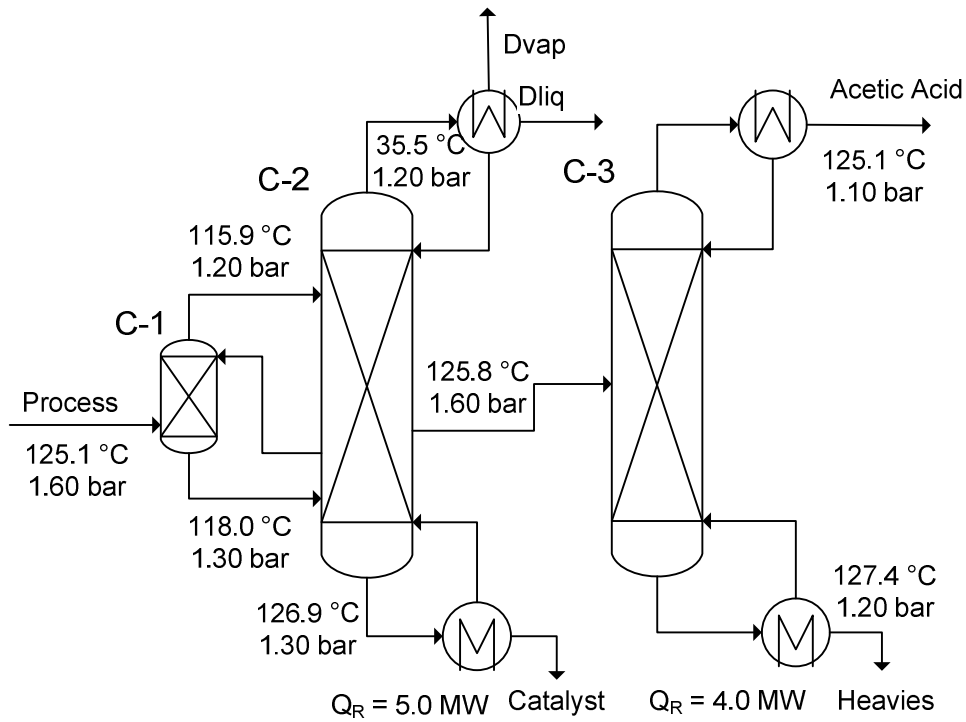


Figure 5. Alternative 3: Petlyuk set-up configuration (C1+C2)+C3

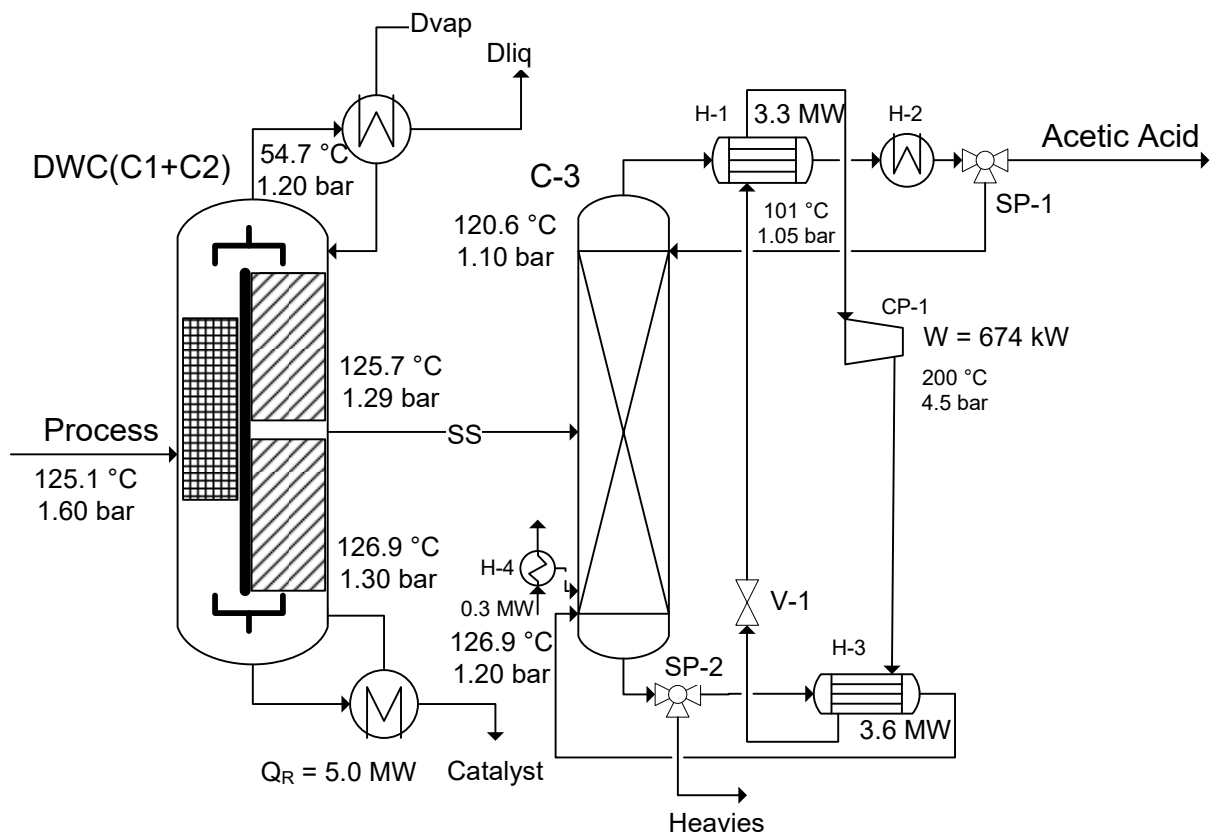


Figure 6. Alternative DWC(C1+C2) + C3 + Heat pump

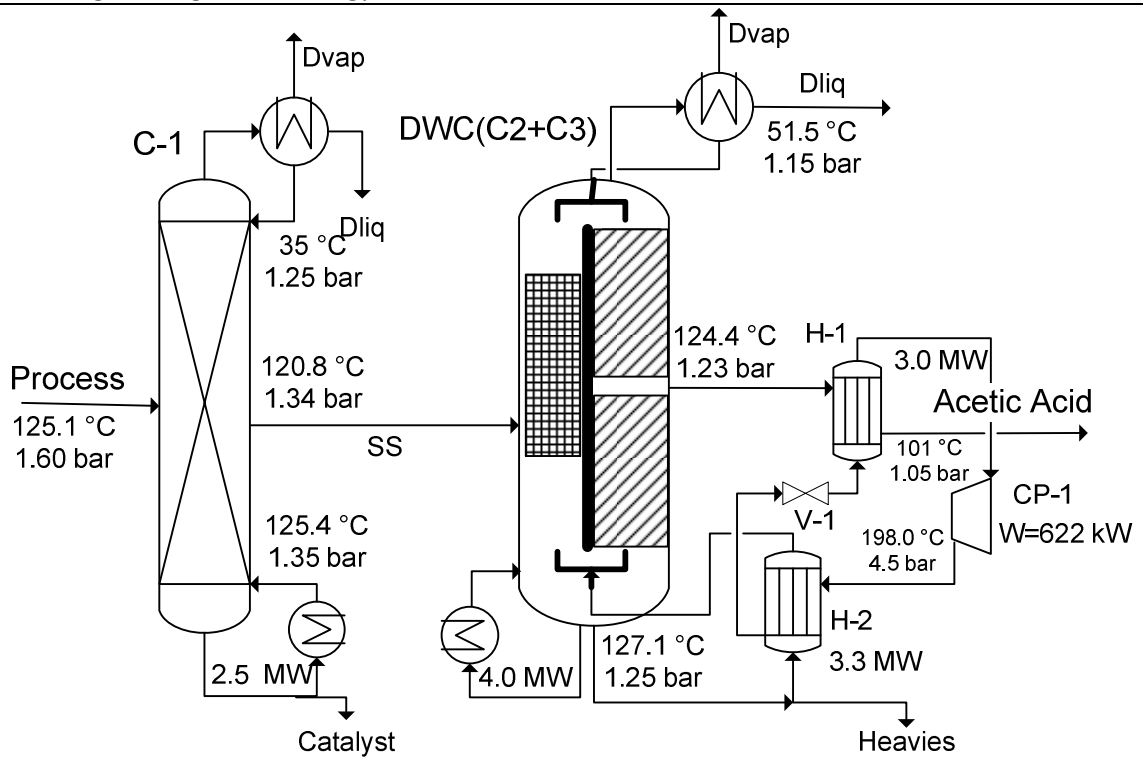


Figure 7. Alternative C1 + DWC(C2+C3) + Heat pump

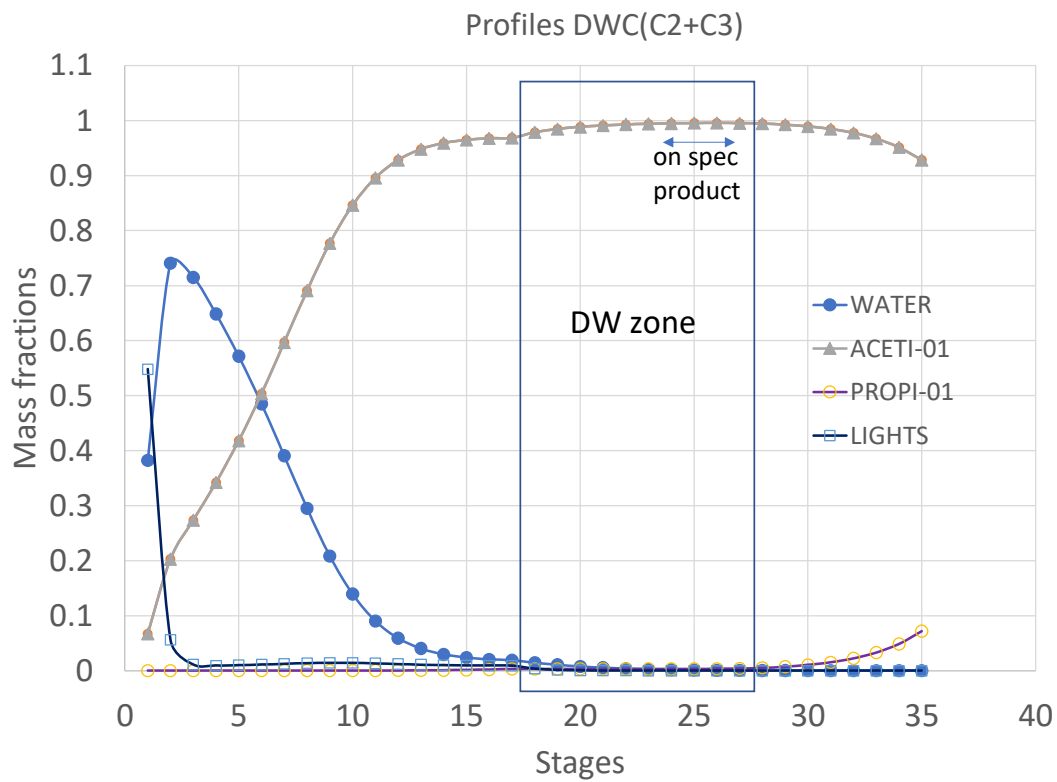


Figure 8. Liquid concentration profile in the DWC (C2+C3)