THERMODYNAMICALLY EFFICIENT DISTILLATION:  
ETHYLENE RECOVERY 

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Abstract  
The problem of recovering ethylene and byproducts from the steam pyrolysis of light hydrocarbons is discussed. Opportunities for improved efficiency using distributed distillation, recycle coupling, heat pumping, and mixed refrigeration are presented. Emphasis is placed upon energy efficiency with potential savings in capital costs as applied to refrigerated processes.

1. Introduction  
Significant savings in utilities may be achieved by using heat integrated distillation in innovative configurations. On a percentage basis, capital savings are somewhat smaller than utility savings; but they are not negligible. The improvements are at the expense of increased complexity, and incur the risk of new technology. However, conventional equipment may be used, and only the configurations changed.

The innovative configurations may be generated by observing thermodynamic inefficiencies in conventional process designs. These are typically apparent in relationships between the primary process variables such as temperature, pressure, and composition. The relationships may be observed through conventional analysis such as McCabe - Thiele diagrams, composite heating and cooling curves, and temperature - composition plots.

Because of the multiple products produced in the production of ethylene by steam pyrolysis of light hydrocarbons and because of the high pressures and low temperatures required for their recovery, ethylene manufacture provides several opportunities for economical process improvements through improved thermodynamic efficiency.

2. Conventional Ethylene Recovery  
Table 1 shows the feeds and products normally encountered in the ethylene recovery process. Both the gas (ethane) and liquid (naphtha) feeds contain about 31% ethylene, but the light and heavy byproducts differ considerably. The pyrolysis reactions are favored by low pressure. However, because of the low boiling points of the products, high pressures and low temperatures must be used for their separation by distillation. High purity is required for both the ethylene and propylene products, and ethylene and ethane have similar boiling points as do propylene and propane. As a result large diameter columns with many trays are required, and these separations are usually accomplished at the end of the recovery process. The recovered products are produced at ambient temperature and pressures sufficient for downstream processing or for a pipeline.

Figure 1 shows a conventional ethylene recovery distillation process (Kniel, et. al., 1980). The feed has been compressed, treated, dried, and partially hydrogenated to remove acetylene. Part of the methane and all of the ethylene and heavier components are separated from the hydrogen and remaining methane by condensation at low temperature. The liquids are then fractionated under pressure into products in demethanizer (DMR), deethanizer (DER), depropanizer (DPR), C2 splitter (C2S), and C3 splitter (C3S) distillation columns.

3. Thermomechanically Integrated Distillation  
As discussed above the C2 and C3 splitter columns are large and expensive, and accurate thermodynamic properties are necessary for their economical design. Figure 2 shows the relative volatility of propylene to propane on isotherms as functions of liquid phase composition. The logarithm of relative volatility is plotted because
it is closely related to the number of stages and the reflux required for the separation. At the high propylene end the relative volatilities are small, and they don’t change much with temperature. This implies that reducing the column pressure, which also reduces the temperature, will not reduce the column size significantly. However, at the high propane end the relative volatilities are larger, and they may be increased significantly by reducing the column pressure. The same phenomenon occurs in the case of ethylene and ethane because of the similar olefin / paraffin interaction between the molecules.

The analysis points toward using dual pressure columns for C2 and C3 splitting with the stripping sections at lower pressures than the rectifying sections. Normally, this would require an extra compressor which would be too expensive and unreliable. However, refrigeration or heat pumping, both of which require compression, must be used for C2 splitting anyway; and heat pumping may be used for C3 splitting. Consequently, there is an opportunity to combine the compression functions using “thermomechanical integration” (Greene et. al., 1994; Manley and Haddad, 1995) as shown in figure 3.

The rectifying section in figure 3 is conventional. However, a few stages below the feed a heat pumped interreboiler is used to partially condense the overhead while simultaneously compressing the vapors from the low pressure stripping section below. A similarly heat pumped reboiler is used to condense additional overhead vapors. Because the relative volatility of olefin to paraffin is much larger in the low pressure stripping section, significantly less boilup is required, and more heat may be used in the interreboiler than in a conventional, single pressure, column. The effect is enhanced because the olefin / paraffin ratios in the feeds generated by pyrolysis are high by design to increase conversion. For a liquid overhead product a small amount of addition refrigeration may be necessary to remove the energy required to drive the compressor. Figure 4 summarizes the advantages of the more thermodynamically efficient process.

4. Distributed Distillation of Ethylene
Another inefficiency inherent in conventional ethylene recovery may be observed in figure 1 by keeping track of the phase changes necessary to process the major (ethylene) component. Ethylene enters the recovery process as a gas, is condensed in the demethanizer feed system, is revaporized in the deethanizer, and is finally recondensed again as a liquid product from the C2 splitter. A total of three complete phase changes must be accomplished for all the ethylene. A similar analysis for other products yields similar conclusions. Propylene, for example, is condensed in the demethanizer feed system, revaporized in the depropanizer, and recondensed again as a liquid product from the C3 splitter. Are all these phase changes really necessary?

Figure 5 shows an “ethylene distributor” column (Conroy et. al., 1996) which separates methane from ethane in the presence of hydrogen while distributing ethylene between the overhead and bottoms products. A preliminary separation of the C3 and heavier components is not shown in the figure. The ethylene distributor column overhead is processed in a downstream demethanizer column, and the ethylene distributor bottoms is processed in a downstream C2 splitter column. In a properly designed process approximately one half of the ethylene in the feed will be distributed through the demethanizer and about one half will be distributed through the C2 splitter. However, the half which passes through the demethanizer must be condensed only once since ethylene product is produced in the demethanizer bottoms. Consequently, the total number of phase changes necessary to produce the ethylene product is reduced, and the thermodynamic efficiency of the process is improved.
5. Recycle Coupling

Figure 6 shows the liquid composition profile for the ethylene distributor column in figure 5. The feed at about -66°F is separated into ethane free methane and ethylene on the top stage at about -70°F and into methane free ethane and ethylene on the bottom stage at about -29°F. However, because of the presence of hydrogen, the condenser must cool the overhead to about -103°F in order to generate the required reflux. This condensing process “remixes” methane and ethylene, which have been more completely separated at the entrance to the condenser; and they must then be “reseparated” in the downstream demethanizer column. A similar phenomenon occurs to a lesser extent in the reboiler at about -28°F where ethane and ethylene are “remixed” and must then be “reseparated” in the downstream C₂ splitter column.

The mixing and separating occurring in the condenser and reboiler of the ethylene distributor column may be eliminated by using “recycle coupling” (Manley, 1996) as shown in figure 7. In this case, the ethylene distributor column is refluxed using a liquid sidedraw taken from the feed stage of the downstream demethanizer, and the ethylene distributor column is reboiled using a vapor sidedraw taken from the feed stage of the downstream C₂ splitter column. Figure 8 shows the effect of recycle coupling on the composition profile in the ethylene distributor column. Remixing is eliminated and consequently the separations required in the downstream demethanizer and C₂ splitter columns are significantly reduced.

In figure 7 the ethylene distributor condenser and reboiler from the figure 5 process have been replaced by an intercondenser on the demethanizer and an interreboiler on the C₂ splitter respectively. This allows the same utilities to be used in both cases. However, because of the improved thermodynamic efficiency when recycle coupling is used, the reflux and reboil flows in the demethanizer and C₂ splitter are smaller in the case with recycle coupling. An added advantage of the figure 7 process is the elimination of the demethanizer reboiler by using overhead vapor from the C₂ splitter to provide reboil vapor.

Figure 9 shows how thermomechanical integration, ethylene distribution, and recycle coupling may be used in a thermodynamically efficient process for the recovery of ethylene from pyrolyzed ethane. The compressed, treated, dried, and hydrogenated gases are cooled, and the C₃ and heavier components are removed in a deethanizer (DER) column. The deethanizer overhead feeds the downstream ethylene distributor column (C₂D), and reflux for the deethanizer is provided through recycle coupling with the ethylene distributor. An interreboiler and intercondenser are used on the deethanizer and ethylene distributor respectively to provide optimum integration with the utility systems. For the same reason, a dephlegmator is used as the demethanizer (DMR) rectifying section. Reboil for the deethanizer is provided through recycle coupling with
the C₂ splitter (C₂S), and the C₂ splitter is thermomechanically integrated with a bottoms heat pump. Finally, the demethanizer is reboiled using overhead vapor from the C₃ splitter. The process shown in figure 9 requires less capital and utilities than the conventional process shown in figure 1 because it is more thermodynamically efficient.

6. Mixed Refrigerant

The thermodynamic efficiency of the recovery process in figure 9 may be further improved by using mixed refrigerants because the cooling curves resulting from the recycle coupling, intercondensing, dephlegmation, and thermomechanical integration are less flat than a conventional process. Figure 10 shows the cooling curve for a typical ethylene condensation process which may be used as a basis for comparing refrigeration processes.

A conventional pure component, multistage, cascaded refrigeration process is shown in figure 11. Pure ethylene refrigerant is used as a refrigerant between about -70°F and -150°F, and the absorbed energy is rejected to pure propylene refrigerant at about -40°F. Propylene is used to absorb energy from the ethylene cycle and to provide refrigeration from about -40°F to +50°F. The energy absorbed by the propylene is rejected to cooling water at about 100°F. When the refrigeration process of figure 11 is used to provide cooling for a process with the cooling curve shown in figure 10, the resulting composite cooling and heating curves shown in figure 12 result.

In figure 12 the condensation of the ethylene and propylene refrigerants is shown by the plateaus at -35°F and +105°F in the cooling curve respectively. The vaporizing refrigerants are shown by the seven plateaus below +90°F in the heating curve. The heating curve for the cooling water is shown between +90°F and +100°F. The sloping cooling curve from about +165°F to about +105°F represents the desuperheating of the compressed propylene vapors. A similar desuperheating curve for the ethylene refrigerant is combined with the ethylene condensation curve from about +54°F to about -35°F. The combined processes require about 220 MMBtu/HR of heat exchange.

Several of the thermodynamic inefficiencies associated with using cascaded propylene / ethylene refrigeration for condensing ethylene are summarized in table 2. Because the ethylene condensation curve is sloping and the refrigerant vaporization curves are flat there is necessarily a nonuniform temperature driving force in the heat exchangers, and the minimum average temperature driving force is limited to about half the temperature difference in refrigeration levels. A closer approach in the heat exchangers would increase heat exchanger cost slightly, but would decrease compressor and operating costs more than enough to compensate.

Similarly, the relatively flat condensation curve for the propylene refrigerant mismatches with the sloping heating curve for the cooling water. This limits the cooling water temperature rise
unless the propylene condensing pressure is raised with commensurately increased compression costs.

**FIGURE 12**
COMPOSITE HEATING AND COOLING CURVES
CONVENTIONAL REFRIGERATION PROCESS

![Composite Heating and Cooling Curves](image)

**TABLE 2**
THERMODYNAMIC INEFFICIENCIES ASSOCIATED WITH CONVENTIONAL REFRIGERATION

| MISMATCH OF PROCESS COOLING AND REFRIGERANT HEATING CURVES |
| MISMATCH OF REFRIGERANT COOLING AND WATER HEATING CURVES |
| IRREVERSIBLE FLASHING THROUGH VALVES |
| LIMITED SELECTION OF REFRIGERANT PROPERTIES |

Although it is not apparent in the figures, partial flash vaporization of the refrigerants through the refrigeration valves contributes to compression costs since the vapors must then be recompressed and recondensed without providing any process cooling.

Finally, there is a limited selection of pure component refrigerants so their properties cannot be optimized for an arbitrary process application. Propylene is used for the high temperature cycle in the conventional refrigeration process because it can be condensed at 100°F and can be practically vaporized as low as -54°F. An even lower vaporization temperature would be advantageous since less heat transfer would be necessary in the cascade interexchanger between the high and low temperature cycles. However, ethane, the next lower boiling pure component becomes supercritical at 90°F and cannot be condensed with cooling water.

**FIGURE 13**
MULTILEVEL, CASCADED, MIXED REFRIGERANT PROCESS

![Multilevel Cascaded Mixed Refrigerant Process](image)

Figure 13 shows a seven level cascaded mixed refrigeration process (Manley, 1997a,b) suitable for providing cooling for a process with the cooling curve shown in figure 10. The high temperature cycle mixed refrigerant comprised of ethylene, ethane, propylene, and propane is completely condensed at 100°F and 525 psia using cooling water. To avoid excessive flashing in the 59°F level refrigeration valve the condensed refrigerant is subcooled simultaneously with the process fluid in a multistream heat exchanger using 59°F level refrigerant as a heat sink. The 59°F level mixed refrigerant pressure of about 338 psia is chosen so that the 59°F level refrigerant stream is about 5°F colder than the subcooled stream, and so that the completely vaporized 59°F level refrigerant is heated to the cooling water temperature of about 90°F. The composition of the mixed refrigerant is chosen so that the refrigerant condenser pressure is a practical maximum of about 525 psia, and so that the heating curve for the mixed refrigerant is approximately linear or slightly convex. The completely vaporized 59°F level mixed refrigerant is mixed with desuperheated compressed refrigerant from the lower levels, and is compressed to the water cooled condenser pressure.

The 59°F level refrigeration loop described above is essentially a conventional single loop mixed refrigeration process operating from 59°F to 90°F and providing refrigeration to cool the process stream from about 100°F to about 64°F. However, the 59°F level also provides refrigerant subcooling for the lower levels and provides fifth stage compression for the combined refrigerants from the lower levels.

Four lower temperature loops at 24°F, -17°F, -60°F, and -105°F are also shown of the high temperature cycle in figure 13. Each of these loops is similar to the 59°F loop, and the entire, five stage, cycle provides refrigeration continuously to -105°F with a single mixed
refrigerant.

A single loop low temperature mixed refrigerant cycle starting with a pressure of about 408 psia and a condensing temperature of about -100°F, which is the lowest process temperature achieved in the high temperature cycle, is used to further cool the process in two steps to -123°F and then to -147°F while simultaneously subcooling the mixed refrigerant. The evaporated refrigerant is then compressed to the condenser pressure and is sequentially cooled and totally condensed by the high temperature cycle.

Figure 14 shows the composite cooling and heating curves when the mixed refrigeration process of figure 13 is used to provide cooling for a process with the cooling curve shown in figure 10. The close temperature approaches are apparent, and the cooling water is heated to about 120°F. About 240 MMBtu/Hr of total heat exchange is required. Because of the subcooling of the mixed refrigerant, this is about 20 MMBtu/Hr more than in the conventional process shown in figure 12. The weighted average temperature driving force in the figure 14 process is less than one half that in the figure 12 process.

Table 3 gives a comparison of several important design and cost considerations for the conventional cascaded propylene / ethylene (CONV) and the proposed cascaded multilevel mixed refrigerant (MLMR) processes. The multilevel mixed refrigerant process achieves large improvements in compressor power, compressor suction volumetric flow, cooling water usage, and cooling water pumping power. However, because of the subcooling some additional heat exchange is required, and the reduced temperature approaches require greater heat exchange area. The power reductions will contribute directly to operating and capital cost reductions, and the reduced volumetric flows will contribute significantly to capital cost reductions. The increased heat exchange and the smaller temperature approaches will greatly increase the heat exchange area for the mixed refrigerant process, and the higher compressor discharge pressures will add somewhat to the equipment costs. The optimal overall process will depend upon an economic balance of these factors. However, the multilevel mixed refrigerant process has the advantage because of its higher thermodynamic efficiency.

7. Discussion

Several opportunities for the improvement of the thermodynamic efficiency of processes designed for the recovery of ethylene and byproducts from pyrolyzed hydrocarbons have been described. As a result the energy efficiency and resulting utilities costs of the process are significantly improved. However, each of these improvements adds additional complexity to the process with associated implications for process control and installation costs.

The process control questions may be addressed through appropriate hold-up volumes placed strategically in the process and through appropriate computer control systems. The installation costs may be mitigated through modularization of several pieces of equipment into a single unit. However, these subjects are beyond the scope of the present discussion. The combined effect is a more economical and reliable operating unit with significantly lower capital and operating costs.

References


