

Industrial Distillation Aspects of Diketene

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Abstract: Large-scale distillation is a challenge in many respects. Particularly difficult is the purification by distillation of a compound with limited thermal stability. This article describes various aspects of these difficulties with some possible solutions. Special emphasis is placed on the collaboration of different disciplines to find pragmatic solutions to these challenges. The purification of diketene in quantities of several 1000 t^a is an excellent example to illustrate the different requirements. Although the distillation of diketene has been carried out by several companies for many years, there are still some aspects that deserve special attention.

Keywords: Diketene · Distillation · Industrial · Large scale · Process safety · Thermal stability



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1. Introduction

Diketene has been a valuable industrial intermediate for many decades, providing an astounding versatile starting material that can be used to produce an impressive number of industrial products in virtually all industrial areas.^[1] This versatility is due to diketene's unique multi-center reactivity, as illustrated in Fig. 1.

This reactivity becomes more apparent when considering the frontier orbitals and the electrostatic charge density shown in Fig. 2.

The use of this unique reactivity is illustrated by example reactions leading to important industrial intermediates and products, as shown in Fig. 3.

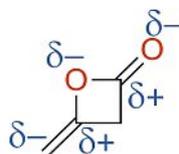


Fig. 1. Multi-center reactivity of diketene.

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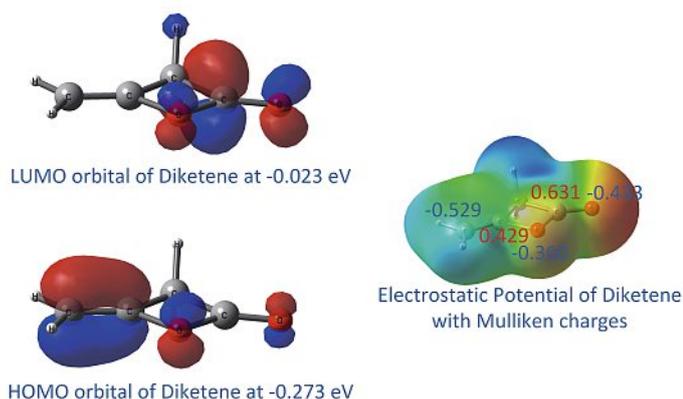


Fig. 2. Frontier orbitals and electrostatic potential calculated at B3LYPD3/6-311+G(2d,p) using Gaussian 16.^[2]

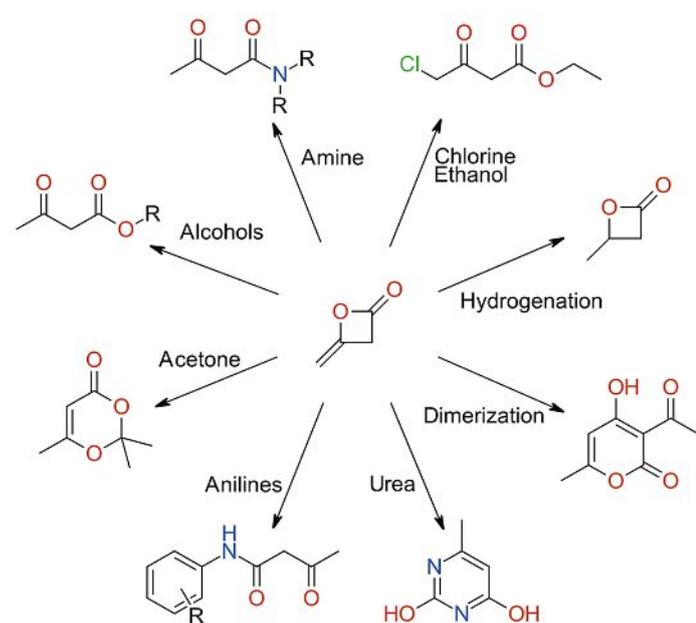


Fig. 3. Industrial reaction products of diketene with various reagents.

More comprehensive applications and products are described in industrially focused reviews.^[3] The reactivities of ketenes and diketenes are described in detail in several monographs and reviews.^[4]

The preparation of diketene is carried out by the dimerization of ketene, whose industrial production is performed by a high temperature process from acetic acid^[3] illustrated in Fig. 4.

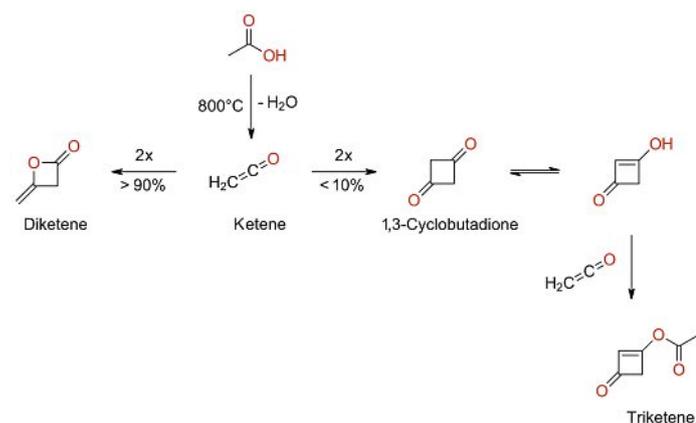


Fig. 4. Reaction scheme of the ketene and diketene production.

This ensures a very cost-effective route to diketene. However, the high reactivity of diketene poses some inherent safety problems. The high decomposition energy was the reason to ban the transport of industrial amounts of diketene outside a production site. The handling and storage of diketene requires a high level of technical expertise with rigorous risk assessments that are reviewed by government authorities in most countries. Despite these technical challenges, the production of diketene can safely be conducted with appropriate measures as illustrated in Fig. 5. The work-up of diketene is an essential part of this production process and is the subject of this article.

2. Stability Considerations

2.1 Thermal Process Safety

Thermal process safety is an essential part of any safety assessment. For the diketene distillation, this aspect is dominant due to the high decomposition energies of 1000 to 1500 Jg⁻¹ material.

The effects of such a high decomposition energy can be seen by assessing the potential for a runaway reaction. The result of such a decomposition of a quantity in the order of tons would be fatal, resulting in a blast wave that would make survival impossible at a distance of 50 to 100 m. This dramatic situation underlines the importance of an extremely careful and well-thought-out risk analysis with correspondingly reliable measures to rule out such an event. The decomposition energies of all treated streams must be addressed throughout.

Careful investigation indicated that the decomposition behavior of the diketene raw material was less stable than that of the purified diketene (see Fig. 6).

It is evident that these differences originate in the contained impurities that are typically present in the raw material. The raw material of diketene was investigated using ¹H-NMR spectroscopy yielding the identification of the impurities shown in Fig. 7.

Since the onset temperature of the raw material is lower than that of the pure diketene, it is obvious that the impurities contained in the diketene are either more unstable themselves or destabilize the diketene. Therefore, we decided to investigate the decomposition behavior of the impurities in more detail. Since most decomposition studies are done by measuring only the thermal effects of any decomposition^[5], the fate of the sample with the resulting decomposition products is typically completely unknown. In addition, the products of most decomposition reactions result in a plethora of compounds, whose specific formation is almost impossible to trace. As a consequence of this, it is notoriously difficult to analytically derive the path of most decomposition reactions and connect it with the resulting thermal effect. However, understanding the course of these decomposition pathways would be highly desirable, as this would provide the basis of knowledge reducing or preventing decomposition. This knowledge is of significant value as it not only provides the basis for improving the distillation yield, but also helps to prevent fouling or damage to plant equipment.

2.2 Decomposition Measurements and Kinetics

After the identification of several typical impurities in the raw diketene (Fig. 7), decomposition measurements at different temperatures (5 °C, 25 °C, 50 °C) were conducted. For this purpose, individual samples were stored at corresponding temperatures over a period of one week and analyzed using ¹H-NMR spectroscopy. According to these measurements, the degradation of triketene was the most significant decomposition detected (see Fig. 8).

The identification of any specific decomposition products of triketene could not be elaborated. The formation of increased amounts of insoluble black solid was indicative of polymerized decomposition products. Nevertheless, the ¹H-NMR measurements allowed the derivation of the decomposition kinetics of

triketene by following its concentration over a period of one week at temperatures of 5 °C, 25 °C and 50 °C (see Fig. 9).

Despite some variations in the measurements, the following reaction rate constants could be derived in reasonable accuracy (see Table 1).

Using an Arrhenius plot with the obtained reaction rate constants yielded the Arrhenius parameters shown in Table 2.

These values imply a half-life of triketene at 50 °C of 16h, at 25 °C of 197h, and at 5 °C of 215 days, respectively.

As there was good indication for the formation of insoluble decomposition products from the triketene decomposition, the kinetic rates can be used to estimate the amount of fouling material that may cause problems over longer periods of distillation.

Table 1. Reaction rate constants of triketene at 5 °C, 25 °C and 50 °C. T = Temperature, $c^{\circ}Tr$ = starting conc. at the investigated Temperature, k = rate constant.

T / °C	T / K	$\ln(c^{\circ}Tr)$ /-	k / s ⁻¹	T ⁻¹ / K ⁻¹	$\ln(k) / -$
5	278.15	-0.445	$3.73 \cdot 10^{-8}$	0.003595	-17.1
25	298.15	-0.465	$9.79 \cdot 10^{-7}$	0.003354	-13.8
50	323.15	-1.35	$1.20 \cdot 10^{-5}$	0.003095	-11.3

3. Physical Property Assessment

3.1 Literature Data

Modelling and simulation are an essential part of process development and optimization in specialty chemicals. This includes

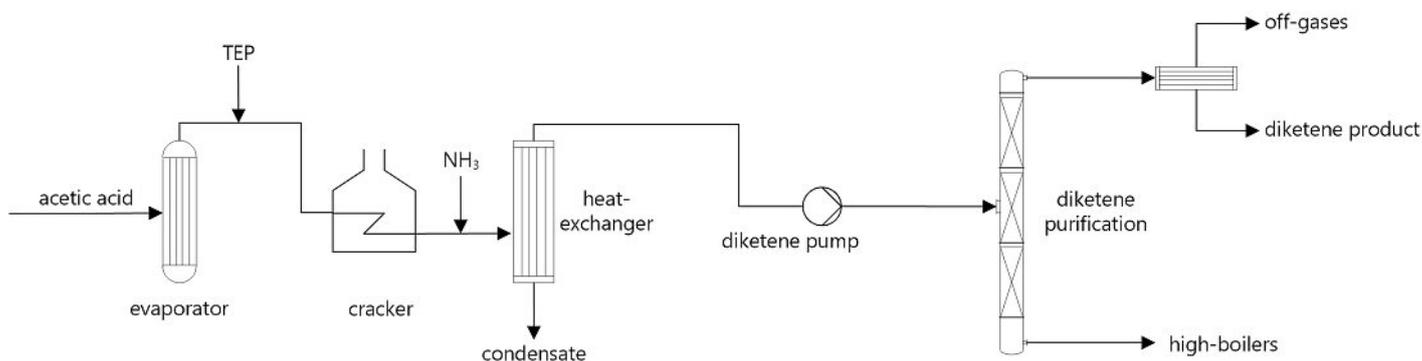


Fig. 5. Schematic setup of a diketene production process. Ketene is formed in the cracker using TEP (triethyl phosphate) catalyst. Subsequently ketene is dimerized into diketene in the diketene pump and purified by distillation (diketene purification).

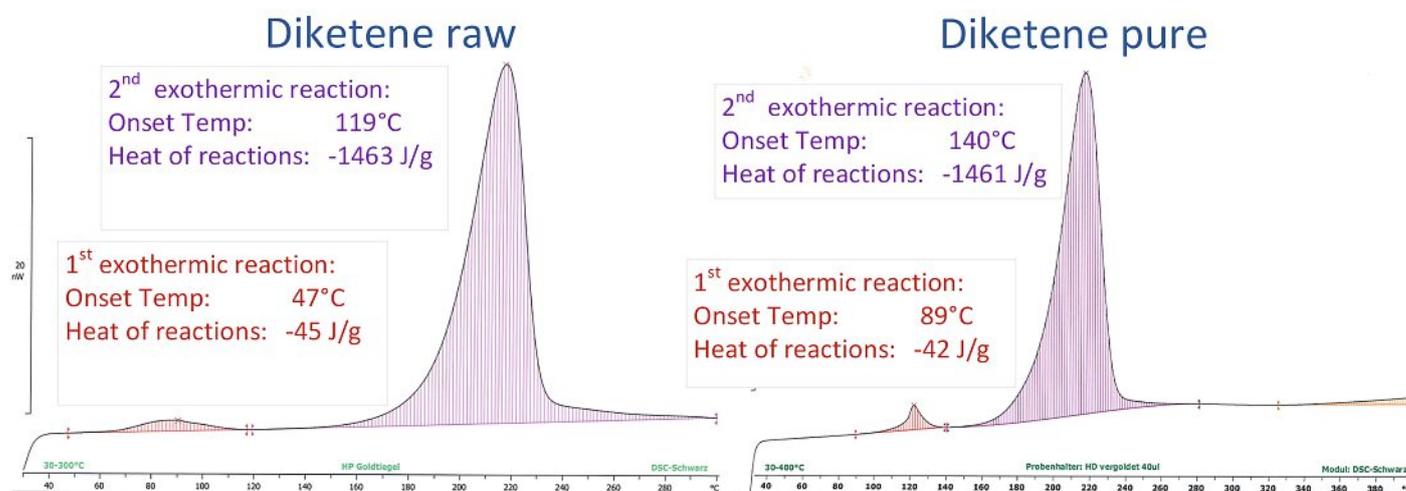


Fig. 6. Dynamic DSC (differential scanning calorimetry) measurements (4 °C min⁻¹) of diketene raw and pure.

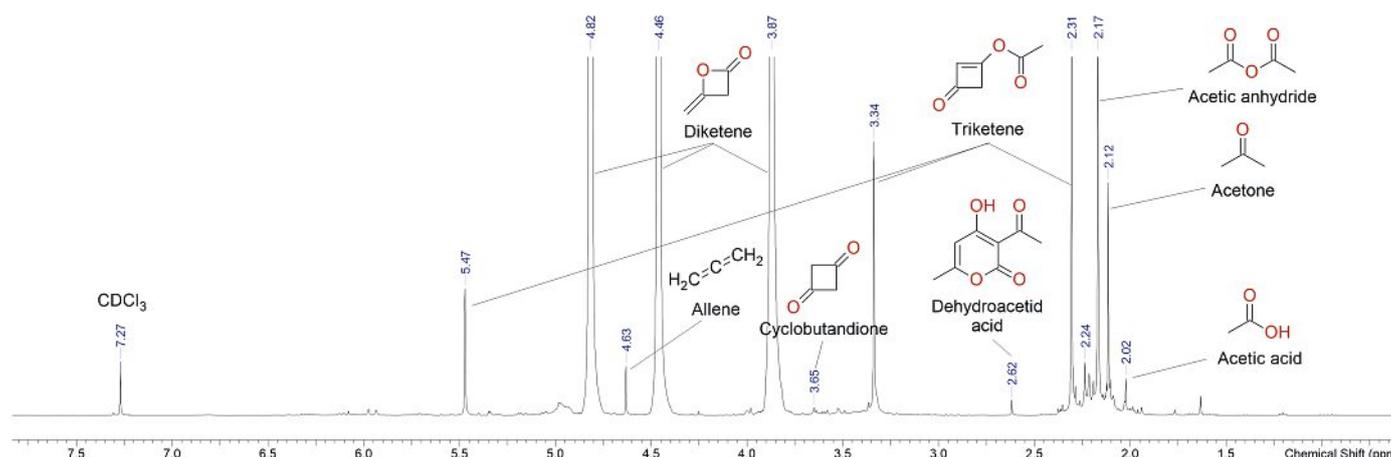


Fig. 7. ¹H NMR spectrum showing the most prominent impurities of the raw product of the diketene synthesis.

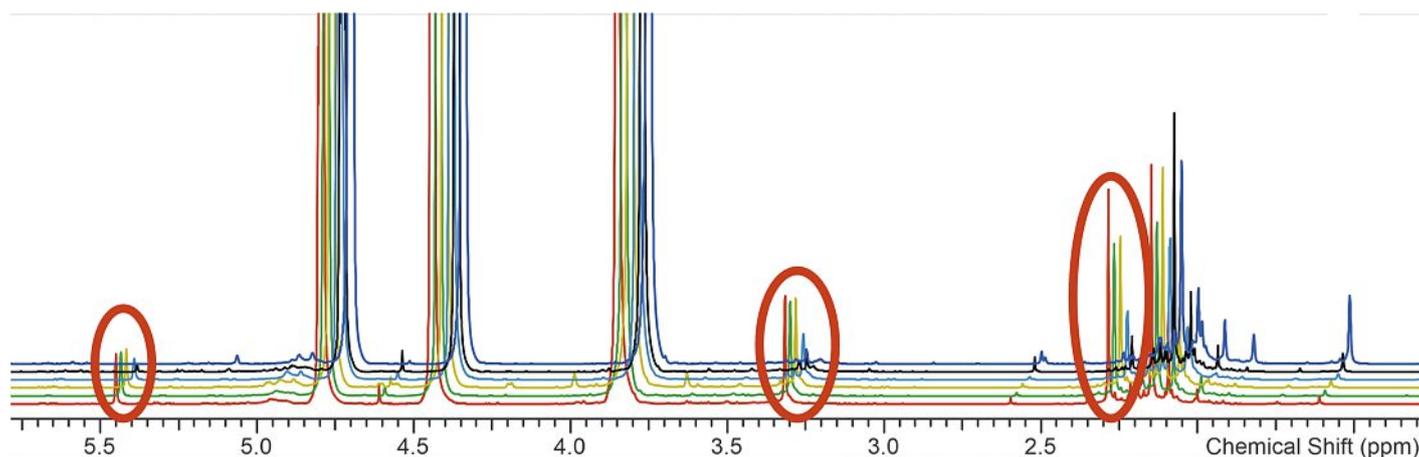


Fig. 8. Changes of the $^1\text{H-NMR}$ spectra of raw diketene at 25°C over a period of 7 days. Red spectrum at the beginning of the measurement sequence, blue spectrum after 7 days. Red circles show the significant changes. All three signals can be assigned to triketene.

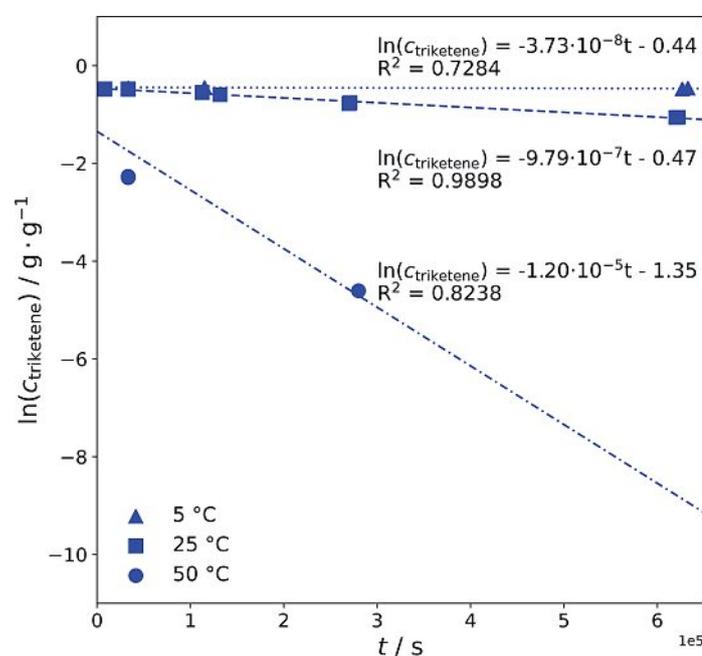


Fig. 9. $^1\text{H-NMR}$ spectrum of raw diketene with identified impurities.

Table 2. Arrhenius parameters for the decomposition of triketene in raw diketene.

A / s^{-1}	E_A / Jmol^{-1}
$4.12 \cdot 10^{10}$	95690

reaction and separation technologies as well as the design, efficiency, and cost aspects of manufacturing processes. In order to achieve a good agreement between simulations and actually performed processes, accurate physical properties of the compounds involved are essential. The most important physical data for the simulation of distillations are boiling points, vapor pressures as well as critical and caloric values.

In addition to pure compound properties, interaction parameters must also be taken into account in order to reliably describe the vapor-liquid equilibrium (VLE). The consideration of all necessary interactions is often a major challenge, since even simple distillation processes involve many compounds with more interactions that increase in the second order with the number of compounds. In almost all practical cases, many interactions are miss-

ing despite the consultation of the most comprehensive literature and database collections (Table 3).

Table 3. Selected physical properties of pure compounds present in the diketene distillation. Boiling point at one atm (T_{boil}), Heat of vaporization (H_{vap}), specific heat capacity at 25°C (c_p) were taken from the DDB.^[6]

Component	$T_{\text{boil}} / ^\circ\text{C}$	$H_{\text{vap}} / \text{kJmol}^{-1}$	$c_p(25^\circ\text{C}) / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
Diketene	126.1	43.1	155.7
Triketene	decomp.	-	-
Polyketene	n/a	-	-
Acetic acid	117.9	23.4	123.9
Acetic anhydride	138.6	48.5	189.8
Acetone	56.3	31.2	126.3

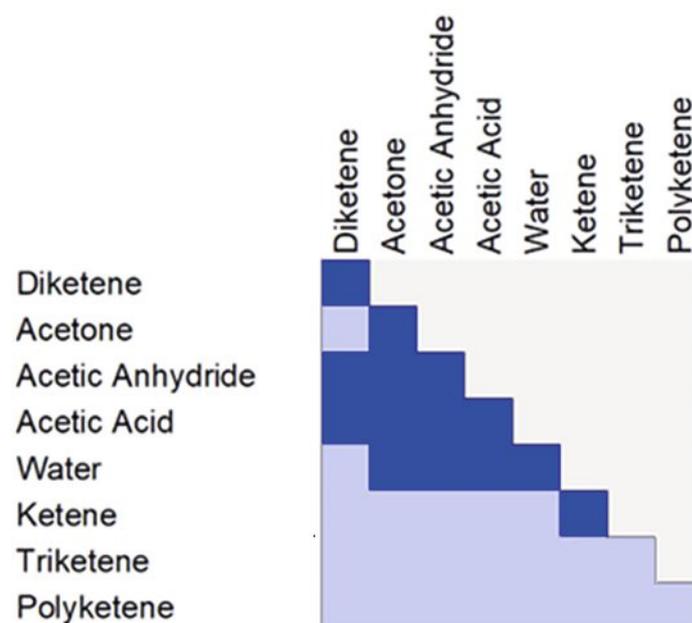


Fig. 10. Interaction matrix with available (blue) and missing (light blue) literature data.

Regarding the distillation of diketene, several compounds with their corresponding interactions were considered as illustrated in Fig. 10. It is easy to see that most of the interactions are unknown, although the Dortmund Databank (DDB)^[6] was consulted with more than 92'000 compounds and 10 million records.

3.2 Measurements

An obvious way to supplement the unavailable data is to perform experimental measurements. Typically, devices such as a Vapor-Liquid-Liquid-Equilibrium (VLLE) measurement cells (see Fig. 11) are used to determine the vapor pressure of pure components and the phase equilibria of multiphase mixtures. The information of the phase equilibria can be used to obtain binary interactions parameters.

Accurate VLE measurements of binary mixtures are time-consuming and challenging. The compounds of interest must be available in accurate purity, they must be sufficiently stable under the measurement conditions, and an accurate analytical quantification method must be available to measure the compositions at the various evaporation or condensation points. It is not surprising that a reasonable number of VLE measurements show significant deviations over different measurements at various locations and at the same place on different dates. Considering the lack of physical properties for all components in a diketene distillation, thermal stability was a major problem in measuring all pure compound properties as well as their interaction parameters. For compounds such as triketene, a VLE measurement was not only meaningless due to the very low thermal stability, but also poses serious safety risks, as an attempt to measure a boiling point would have resulted

in an explosion. Thus, alternative methods were required to derive information on the phase equilibria.

3.3 Filling the Gaps with Predictive Models COSMO-RS^[8]

In cases where VLE measurements are not possible or difficult to obtain, predictive methods can be used instead. Many different predictive methods are available. These can be grouped into purely predictive and so called semi-predictive methods. Examples from the latter group are the UNIFAC group contribution method,^[9] predictive equation of state (PSRK, VTPR),^[10] NRTL g^E -models^[11] with UNIFAC-family group contributions and PC-SAFT.^[12] Examples of purely predictive methods are the COSMO-RS^[8]/COSMOtherm^[13] utility and molecular dynamics techniques.^[14]

Many semi-predictive models rely on experimental correlation techniques to fit a thermodynamic principle with several parameters and applying this fitted principle to a new system in question. This approach is typically very fast and accurate when the new system has a similar chemistry to the fitting data set. However, if the chemistry is substantially different from any compound used in the fitting data set, the prediction may fail completely. This is even more pronounced if the considered compounds are highly polarized and form strong intermolecular interactions. If there is no possibility to validate the predictions, for example due to the lack of available experimental data, it is virtually impossible to estimate the accuracy of these predictions. For purely predictive models, which rely almost entirely on *ab initio* principles, a larger deviation from the observed physical property should be anticipated. The degree of deviation, however, is likely to be similar for all types of compounds. Hence, these purely predictive models (*ab initio* methods) have great generality with some compromise in accuracy.

Considering the compound set in a diketene distillation, semi-predictive methods such as UNIFAC or NRTL g^E -model with UNIFAC group contributions are not possible for several components due to the lack of implementable functional groups. The use of the COSMO-RS^[8]/COSMOtherm^[13] utility for the rather exotic compound composition of the diketene distillation proved to be a valuable method. The compromise in accuracy from the purely predictive models can be significantly reduced by adding pure compound boiling points if available. Fig. 12 illustrates the



Fig. 11. Arxada installation of VLLE measurement cell by Illudest.^[7]

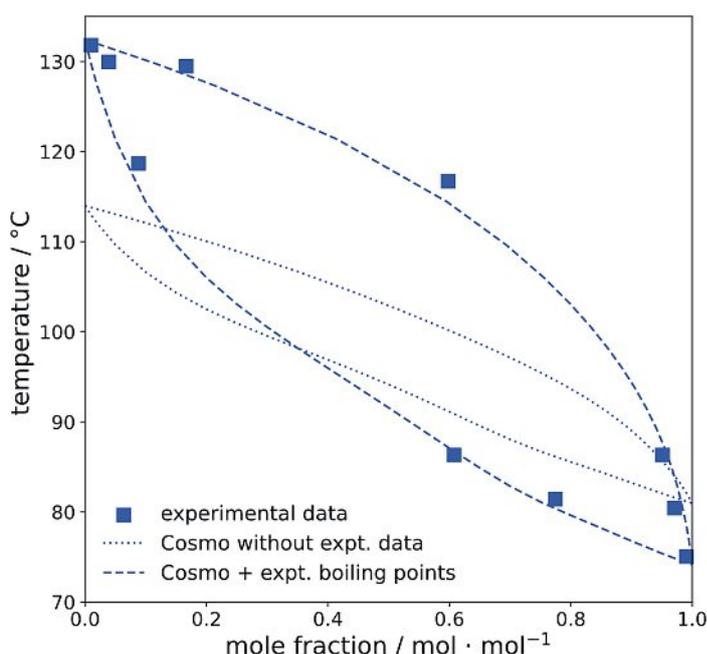


Fig. 12. Predicted vs experimental VLE using COSMO-RS^[8]/COSMOtherm^[13] for an Arxada mixture LB/HB without experimental input and with the addition of 2 pure compound boiling points. LB and HB are abstracted Arxada compounds.

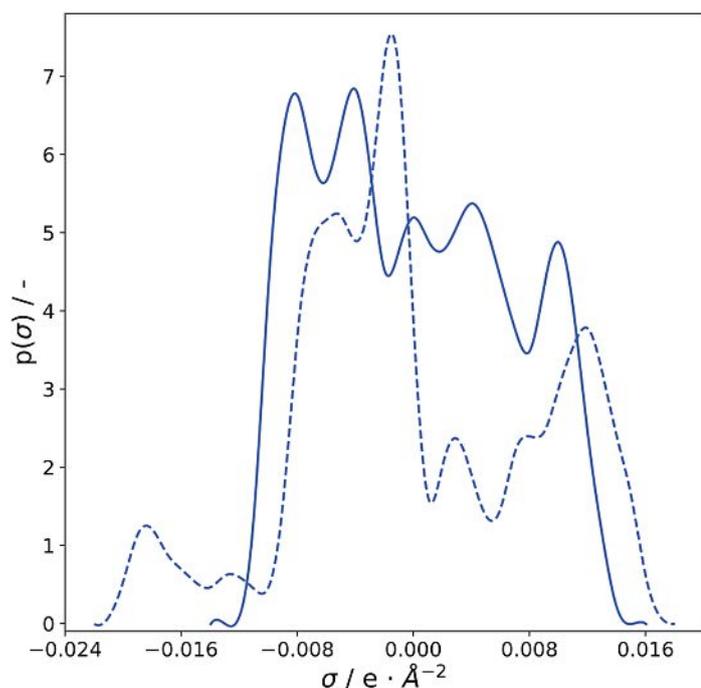


Fig. 13. Sigma profile of diketene (solid) and acetic acid (dashed).

improvement of the VLE prediction for a model system by adding the two pure component boiling points in comparison to the purely predicted VLE.

The rather special chemical properties of diketene are reflected by the electrostatic charge potential (ESP) as shown in Fig. 2. The sigma profile shown in Fig. 13 is derived from the ESP by correlating the abundance ($p(\sigma)$) and its charge density. This sigma profile is then used for statistical thermodynamic calculations using the COSMOtherm^[13] utility allowing the calculation of a variety of physical properties within a very short time (seconds). In this way, the calculation of the T,p,x -diagram of acetic acid and diketene shown in Fig. 14 can be obtained in straight forward way.

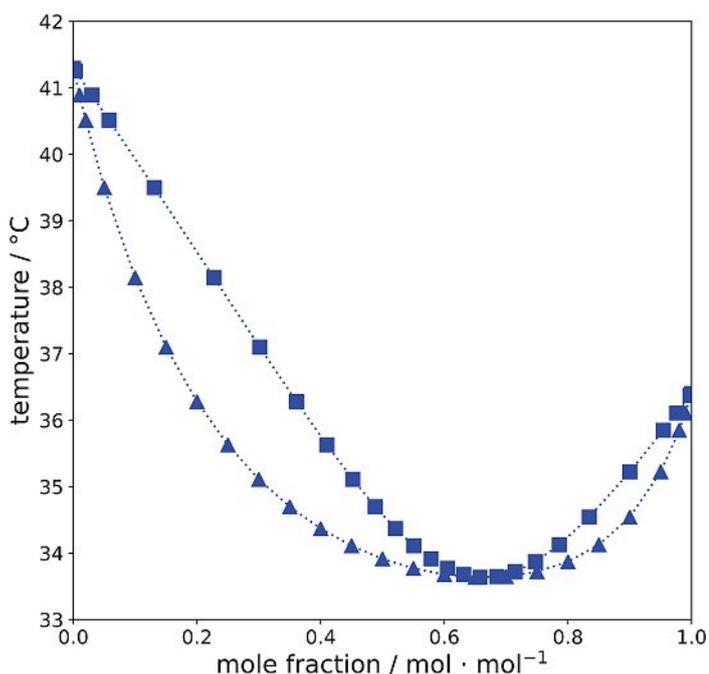


Fig. 14. T,p,x -diagram of the mixture acetic acid/diketene (triangles = dew-line, square = boiling-line) at a pressure of $p=50$ mbar generated with COSMOtherm.^[13]

As expected, methods that derive physical properties from purely physical constants (= *ab initio* methods), such as COSMO-RS^[8]/COSMOtherm,^[13] offer advantages for the prediction of physical properties for rather specialized or exotic compounds as these are likely not available and hence not included in a fitting data set for UNIFAC group contribution methods. Considering the distillation of diketene, these *ab initio* methods are of particular value, as many of the compounds in consideration show strong interactions and experimental measurements are difficult to obtain.

Using the COSMO files (ESP) of the components present in the diketene distillation, binary VLE data (in this case, T,x,y -data at constant pressure) were estimated using the COSMOtherm^[13] utility. These plots were used to perform an NRTL regression, which allowed the physical properties to be imported into the simulation tool ChemCAD.^[15]

The great challenge of predicting the physical properties of compounds with non-readily occurring or highly polarized structures is reflected in the great efforts that are still going on to develop methods using the COSMO-RS^[8] solvation models and to derive increasingly accurate predictions.^[16]

4. Fouling

Distillation of thermal labile reaction mixtures and products is often accompanied by the formation of solid deposits known as fouling. Fig. 15 illustrates an example of extensive fouling in industrial equipment.

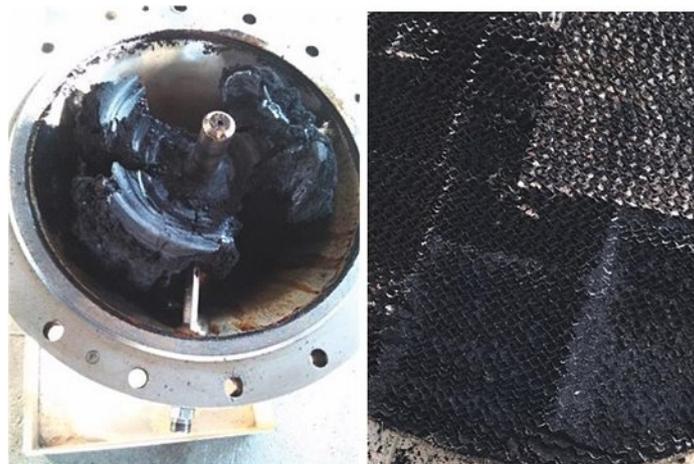


Fig. 15. Extensive fouling example of a thin film evaporator (left) and column internals (right).

Stability measurement of the raw diketene reaction mixture indicated that triketene was the major compound undergoing decomposition even at moderate temperatures below 50 °C. Consultation of the analytical data revealed that no equivalent amount of decomposition products could be quantified. Since the formation of solid material was apparent, severe fouling of this material would be expected when subjected to fractional distillation. One way to minimize this fouling was to flash the raw product at the beginning of the workup process. Such flash distillation would consist of evaporating and condensing all reasonably volatile compounds as much as possible, for which a thin film evaporator can be used. The setup of such a flash operation with subsequent fractionated distillation steps for the removal of light boilers and the isolation of the diketene product as distillate was an obvious workup setup (see Fig. 16). This was investigated by rigorous simulation. In addition to reducing fouling, the removal of easily decomposable compounds had a stabilizing effect on the flash distillate, increasing safety aspects of the distillation process.^[3]

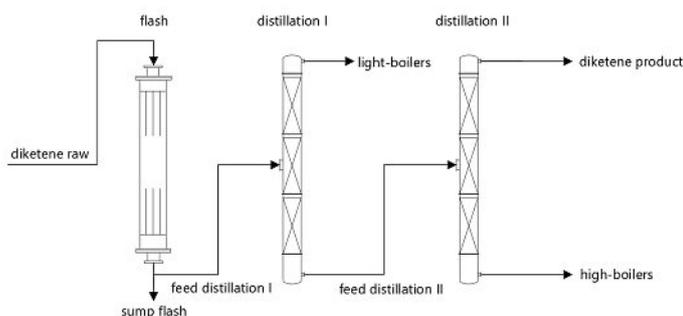


Fig. 16. First setup of a diketene workup process by distillation.

5. Simulations

The first process setup (Fig. 16) was investigated using the ChemCAD^[15] flowsheet simulation tool. This allowed detailed insight into the thermodynamic relations as well as the resulting concentration relations of all streams and units. Hence, it was possible to estimate the predicted quality of the processed product, the amounts of waste streams and the energy consumption. The quality of this estimation depended strongly on the quality of the physical properties and the setup of the simulation flowsheet with all unit specifications. The physical properties were collected from the literature and combined with results from COSMO-RS^[8]/COSMO-therm^[13] modeling as discussed above (see section 3.1 Literature data and 3.3 Filling the Gaps with Predictive Models *COSMO-RS*).

The flowsheet setup shown in Fig. 17 was used in the ChemCAD simulation to reflect the projected diketene workup. The flowsheet of a ChemCAD simulation required the introduction of some additional or separate equipment to cover all aspects that might occur within a single unit in a production plant. The columns were arranged in a sequence. To reproduce the reactions (decomposition of triketene) in the flash evaporator, a reactor was added to the model to emulate the reaction in this unit (see Fig. 17). This reactor was not part of the real process.

To validate the quality of the simulation, experimental measurements are typically used for comparison. A good agreement would confirm the use of an adequate flowsheet setup and a good quality of the physical properties.

6. Validation

Validation of a simulation model is an essential part of the workflow when creating it. This is particularly important when the physical properties are difficult to obtain or when reactions may occur during distillation. The workup of crude diketene was challenging in this respect, as not only the physical properties were difficult to obtain, but decomposition reactions also occurred during the workup process. Therefore, validation was of great value to confirm the predictions of the physical properties as well as a general validity of the simulation.

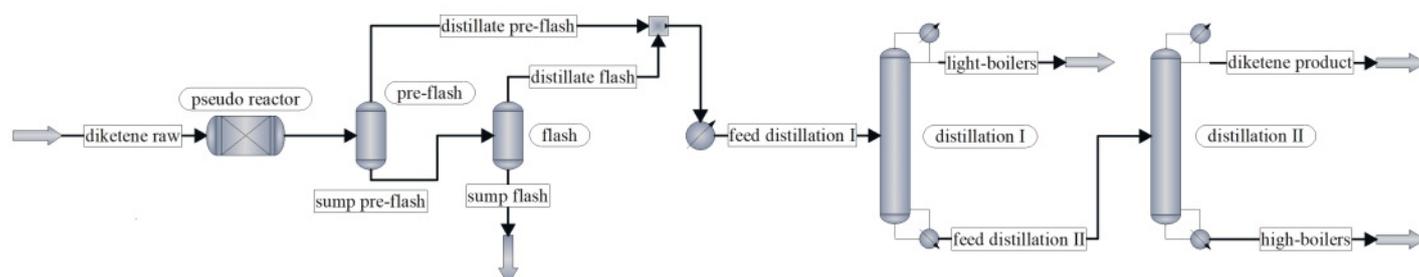


Fig. 17. Flowsheet setup the first diketene workup process.

Using the first setup of the diketene purification, the concentrations of the raw diketene, the flash distillate, the sump of the flash distillation, as well as the diketene product were carefully analyzed and compared with the concentration values derived from the simulation (Fig. 18). The largest deviation was obtained in the sump stream of the flash distillation. This was not surprising, as the analysis of the decomposition products, labeled as polyketene, were known to be difficult. Since the typical GC measurements were not reliable for process streams containing non-volatile compounds, ¹H-NMR measurements were used in addition. For thermally labile compounds such as diketene or, even more dramatically, triketene, GC analysis must be used with caution. Nevertheless, the concentration deviations obtained from the simulation-measurement comparison are in very good agreement. Deviations with less than 1 % indicate that all significant parameters and physical properties are properly addressed.

The temperature profiles in the distillation columns were used as a second measure for validation. The temperature profiles can be reliably compared with the measured values in most distillation columns, since several temperature measurements are usually installed in almost every distillation column. In the case of the first workup setup, distillation I had three and distillation II had five reference temperature measurements, returning values as shown in Fig. 19.

The deviations of the temperature profiles were found to be rather small, indicating a good agreement between simulation and measurement as shown in Table 4 for distillation I and in Table 5 for distillation II.

By confirming good agreement between the simulation and the measured values, the validated model became a valuable starting point for estimating new process setups that allowed the optimization of quality requirements for some customers and the corresponding production costs. These were determined by the factor's distillation yield, throughput, energy consumption, and the depreciation cost of the investment required.

7. Distillation Setups and Evaluations

The quality of a product is usually related to its costs. While better quality is desired in almost all cases, the costs of the product should be as low as possible. In a number of cases, compromises in the quality can be made in favor of the production costs if the quality still fulfills the requirements of the customer. This compromise allows the product to be provided at a reduced cost with eventually reduced energy consumption.

In order to find ways achieving such desired trade-offs, the validated work-up model was used to test several distillation setups. The application of the model provided a good estimate of the quality to be expected with the setup in question. The design of the setup provided information on the required capital investment (CAPEX) and allowed an estimate of the effort required to produce the desired material, known as operational costs (OPEX).

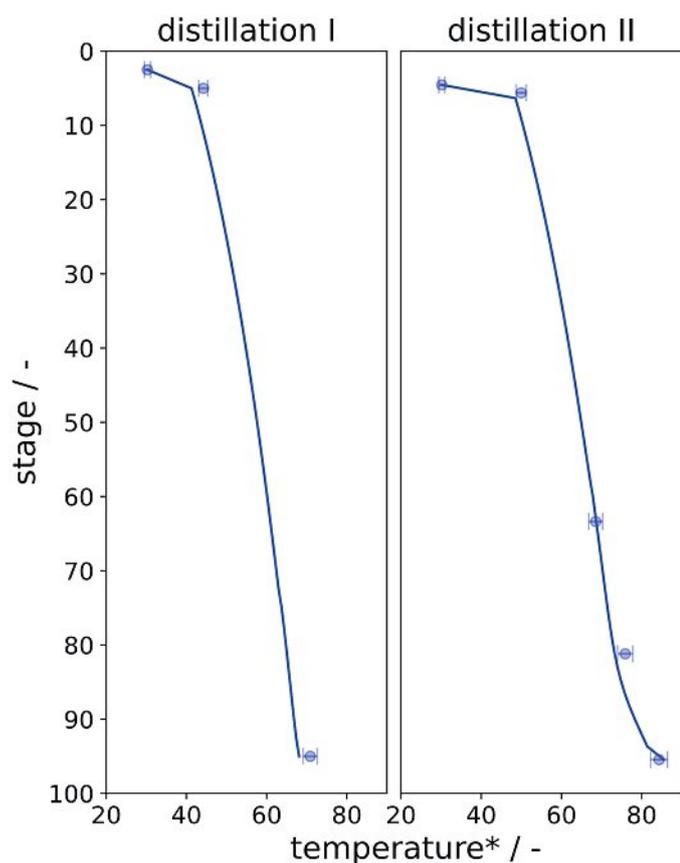


Fig. 18. Comparison of measured and simulated values. The temperature as well as the mass flows are normalized due to regulatory reasons.

Two quite distinct setups illustrating rather extreme situations are described in the following paragraphs: 7.1 CAPEX optimized setup and 7.2 Quality focused setup.

7.1 CAPEX Optimized Setup: Flash – Partial Condensation of the Light Boilers

One critical specification point was the content of acetone in the diketene product for some applications. A straightforward way to remove acetone was to apply partial condensation. This was accomplished in the step of flash distillation. Partial condensation was suitable to remove a large part of the acetone, as the boiling points of acetone and diketene have a reasonably large difference of nearly 70 K with a large curvature of the VLE as shown in Fig. 20.

A suggestion for a CAPEX optimized distillation setup is illustrated in Fig. 21 using partial condensation for the light boiler removal. Considering the physical properties of the compounds involved in the flash distillation, a zeotropic system could be concluded, *i.e.* no technically demanding separation task was expected for the efficient removal of acetone from the flash distillate. Since many possibilities exist to realize a partial condensation in a plant, the simulation setup of this approach (see Fig. 22) was carried out using two flash units in a serial mode. This allowed a better mapping of different realizations in the plant. The amount of diketene drawn into the light-boilers depended on the conditions and the realized setup in the plant. The aim of the simulation setup in Fig. 22 was to find conditions maximizing the removal of acetone while minimizing the loss of diketene.

Although this setup would always lead to reduced distillation yield for diketene with a compromise on acetone content, the required investment would be relatively low compared to more complex scenarios. The operating parameters were adjusted in such a way that the diketene product from the distillation would fulfill the quality requirements. This could be achieved by clever adjusting the operating parameters of the two flash units as well

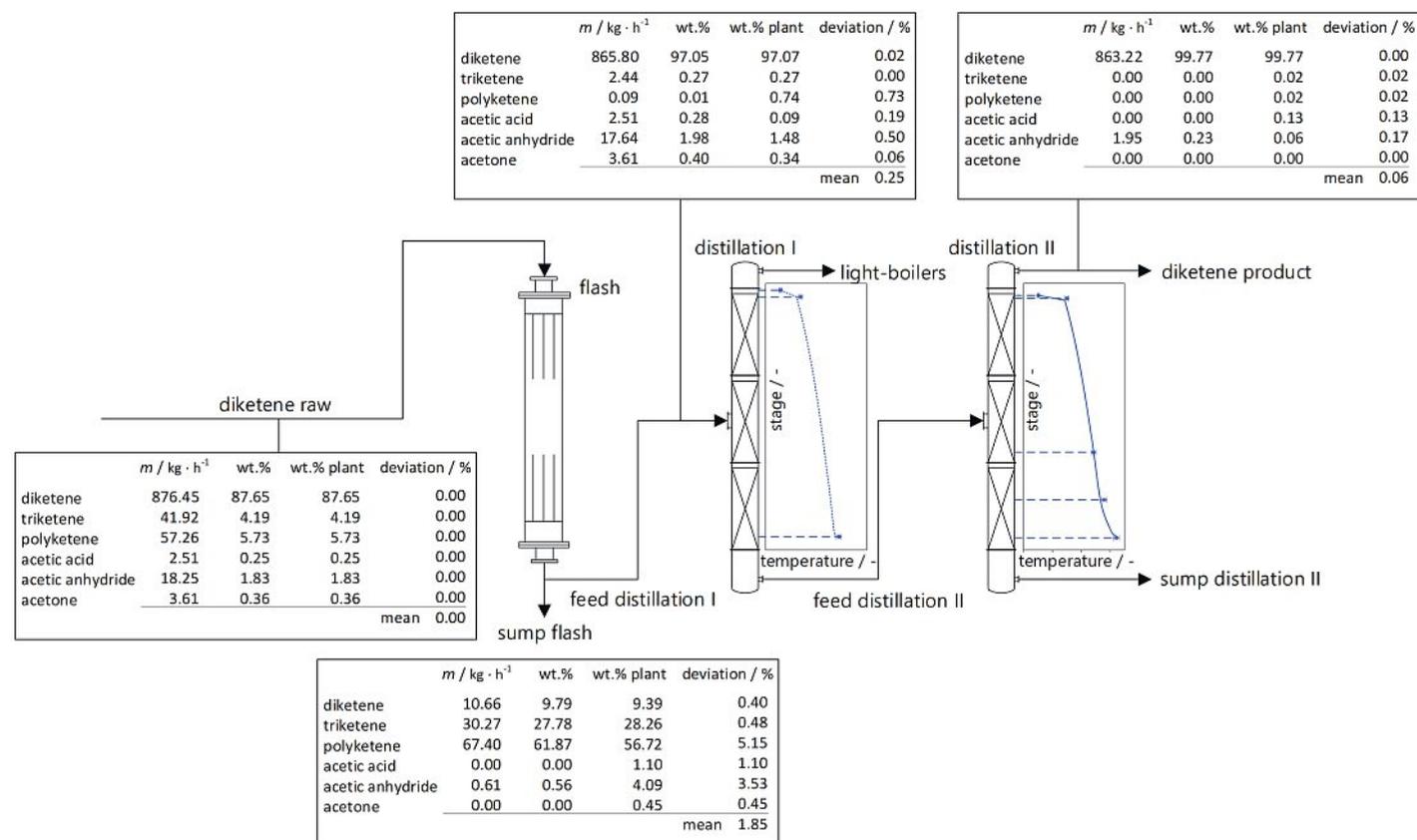


Fig. 19. Temperature profile over the columns of distillation I and II. line: simulation, points: measurements. *Values of the temperature profile was normalized due to confidentiality reasons.

Table 4. Temperature profile in distillation I with simulated and measured values.

stage*	measurement*	simulation*	deviation*
No.	T / °C	T / °C	T / °C
2	30.3	30.3	0.0
5	44.2	41.3	3.0
95	70.9	68.1	2.8

*Values were normalized due to confidentiality reasons.

Table 5. Temperature profile in distillation II with simulated and measured values.

stage*	measurement*	simulation*	deviation*
No.	T / °C	T / °C	T / °C
2	30.2	30.2	0.0
3	50.0	48.5	-1.4
62	68.5	68.7	0.1
73	75.9	73.3	-2.6
81	84.3	85.5	1.2

*Values were normalized due to confidentiality reasons.

as the partial condenser. This design allowed the separation of acetone to a reasonable extent, so that diketene in relatively high purity could be obtained, albeit with a reduction in yield. A semi-quantitative assessment of this setup would lead to the evaluation shown in Table 6.

7.2 Quality Focused Setup: Flash – Dividing Wall Column Scenario

To achieve the highest possible quality, the separation of the diketene product as middle boiler would be ideal. A preceding flash distillation removing the highly unstable triketene would still be necessary as otherwise decomposition of the triketene

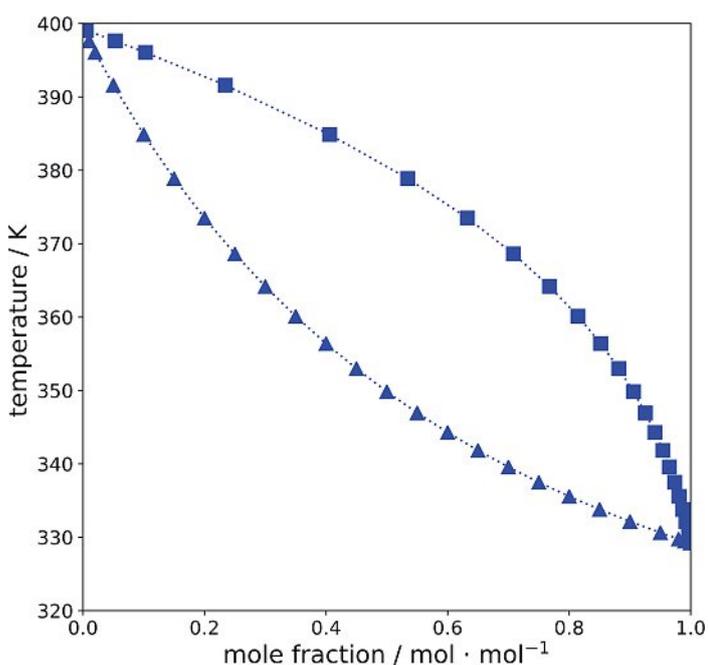


Fig. 20. T,p,x -diagram of the mixture diketene/acetone (triangles = dew-line, squares = boiling-line) at a pressure of $p=1.0125$ bar generated with COSMOtherm.^[13]

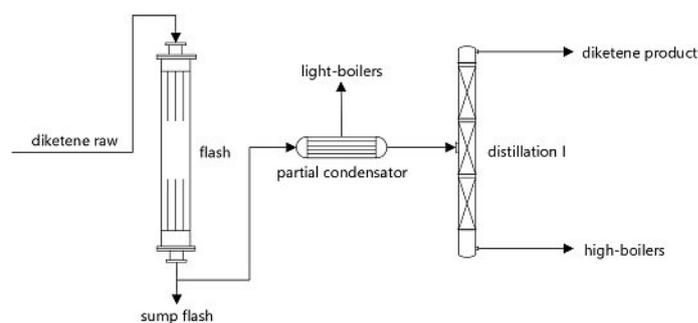


Fig. 21. CAPEX optimized setup.

would lead to clogging problems in the separation columns. An obvious setup for this would be to use two columns: one for light boiler removal and one for high boiler removal. A much more efficient approach doing this would be to use a dividing wall column (Fig. 23) as demonstrated elsewhere.^[17]

Table 6. Semiquantitative assessment of the CAPEX optimized setup.

Quality	+
Yield	-
CAPEX	++
OPEX	+
Energy	-

Using a dividing wall distillation concept, the middle boilers (this would be diketene in our present example) can be directly isolated with high purity and yield. The dividing wall column concept has several key advantages over a two-stage distillation setup: three high purity products can be obtained in one column, lower CAPEX costs compared to a two-stage setup, lower OPEX costs due to lower energy consumption and reduced thermal stress on the product, improved safety aspects and increased distillation yield.

To simulate a dividing wall column concept using ChemCAD, a thermodynamically equivalent variant must be used, as a dividing wall column setup is not available by default in this software.^[18] The appropriate flowsheet setup in ChemCAD is given in Fig. 24. Using the physical properties of the validated simulation and transferring them to the dividing wall distillation setup, the simulated results clearly showed the advantages of this setup for the workup of diketene. A very good diketene quality and yield with a relatively low energy consumption in a simple operation mode could be realized for a medium investment. The corresponding assessment is shown in Table 7.

8. Conclusion

Industrial-scale work-up of a thermally labile reaction mixtures present a number of challenges. These challenges encompass safety issues, fouling, distillation setup limitations, yield reduction, quality requirements, as well as capital and operating cost concerns. To address all these challenges, the workup process requires considerations from multiple disciplines and the integration of this knowledge into a workup process.

The workup of diketene was a very challenging example where the knowledge of chemistry and technology needed to work well together to perform a safe purification. In this way, it was not sufficient to measure the thermal safety of the process by evaluating the thermal signals solely. Valuable insights could be drawn from investigating decomposition by studying stability measure-

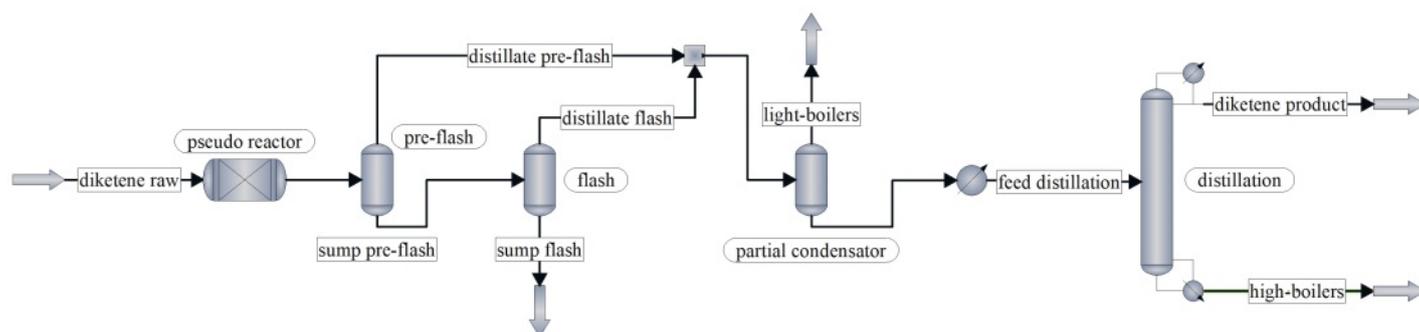


Fig. 22. ChemCAD flowsheet setup of the CAPEX optimized setup.

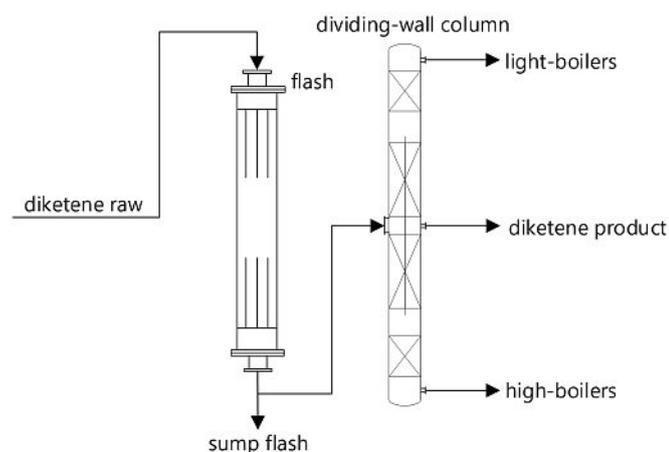


Fig. 23. Quality focused setup using a dividing wall column.

ments using $^1\text{H-NMR}$ spectroscopy in addition to DSC (differential scanning calorimetry) measurements. Detailed knowledge of the behavior of diketene streams under thermal stress allowed the proposal of adequate distillation setups. These distillation setups were aimed to minimize decomposition and fouling effects producing pure diketene in a quality that meets the requirements of subsequent use. Not only quality aspects were taken into account individually, but a number of criteria related to product quality were also considered simultaneously and evaluated in a multivariate manner.

A powerful model was needed to efficiently and simultaneously quantify process criteria such as yield, quality, CAPEX, OPEX, and energy consumption. This was developed by collecting and

Table 7. Semiquantitative assessment of the Quality optimized setup using a DWC.

Quality	++
Yield	++
CAPEX	-
OPEX	+
Energy	+

calculating accurate physical properties and using them within a simulation model setup in ChemCAD. Although not all physical properties and their interactions were obtainable from literature or measurements, smart ways were found to combine experimental and calculated values. A key contribution to complement missing physical parameters and interactions were made by using *ab initio* calculated electrostatic potentials with the COSMO-RS^[8] solvation model and performing statistical thermodynamics on sigma profiles derived from these electrostatic potentials using the COSMOtherm^[13] utility. This technique allowed us to fill in all the missing physical properties and to assemble a robust and accurate simulation model of an example diketene distillation setup. The obtained values were carefully compared with measurable process parameters such as concentrations and temperatures. A very good agreement between the predicted and measured values confirmed the accuracy of the simulation model. Using the parameters of this model, additional distillation setups could be evaluated with respect to yield, quality, CAPEX, OPEX and energy consumption. This evaluation was exemplified using two distillation setups with different emphasis on CAPEX and quality.

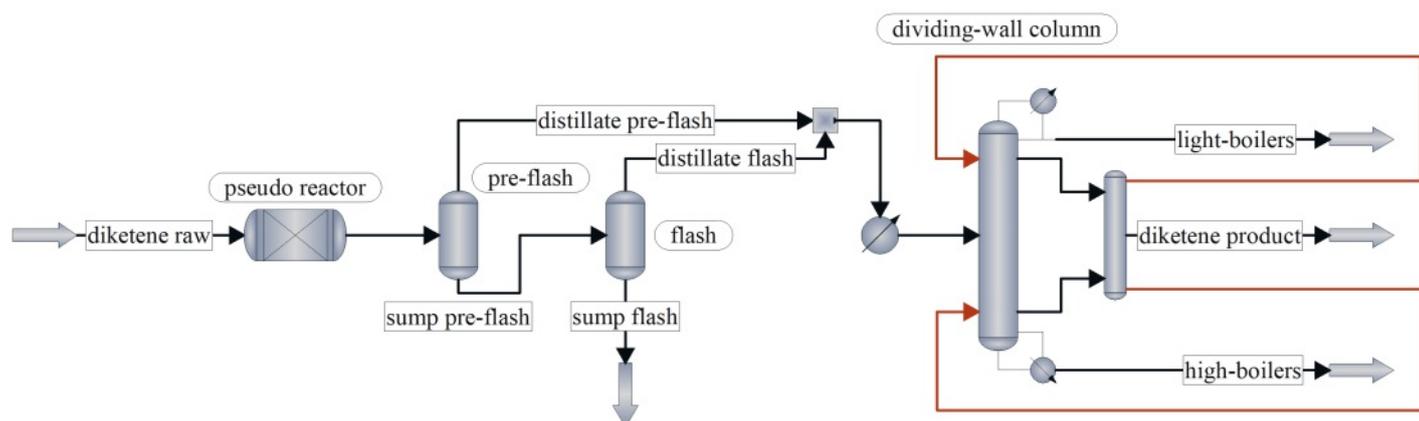


Fig. 24. Flowsheet setup of a flash-distillation followed by a fractionated dividing wall column distillation.

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Software Tools

Turbomol: <https://www.3ds.com/products-services/biovia/products/molecular-modeling-simulation/solvation-chemistry/turbomol/>

Gaussian: <https://gaussian.com/>

COSMOtherm: <https://www.3ds.com/products-services/biovia/products/molecular-modeling-simulation/solvation-chemistry/biovia-cosmotherm/>

Seeq: <https://www.seeq.com/>

ChemCAD: <https://www.chemstations.com/CHEMCAD/>

PI-Server: <https://www.aveva.com/en/products/aveva-pi-system/>

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