

# ENGINEERING PRACTICE

VOLUME 3 NUMBER 10

JULY 2017

## SPECIAL FEATURES

**The Economic Advantage Added by Specialized  
Knowledge of Distillation Fundamentals**

**How Many Pressure Relief  
Devices (PSDs) Do you Have Venting to Atmos-  
phere? Are They Safe?**

**Accurate Prediction of Phase Equilibrium Proper-  
ties Using Peng Robinson Cubic Equation of State**



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VOLUME 3  
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INTERNATIONAL ASSOCIATION OF  
CERTIFIED PRACTICING ENGINEERS

## ABOUT

International Association of Certified Practicing Engineers provides a standard of professional competence and ethics. Identifies and recognizes those individuals that have meet the standard. And requires our members to participate in continuing education programs for personal and professional development.

In addition to insuring a professional level of competency and ethics the IACPE focuses on three major areas of development for our members: Personal, Professional, and Networking.

## HISTORY

The International Association of Certified Practicing Engineers concept was formulated by the many young professionals and students we meet during our careers working in the field, running training courses, and lecturing at universities.

During question and answer sessions we found the single most common question was: What else can I do to further my career?

We found, depending on the persons available time and finances, and very often dependent on the country in which the person was from, the options to further ones career were not equal.

Many times we found the options available to our students in developing countries were too costly and or provided too little of value in an expanding global business environment.

The reality is that most of our founders come from countries that require rigorous academic standards at four year universities in order to achieve an engineering degree. Then, after obtaining this degree, they complete even stricter government and state examinations to obtain their professional licenses in order to join professional organizations. They have been afforded the opportunity to continue their personal and professional development with many affordable schools, programs, and professional organizations. The IACPE did not see those same opportunities for everyone in every country.

So we set out to design and build an association dedicated to supporting those engineers in developing in emerging economies.

The IACPE took input from industry leaders, academic professors, and students from Indonesia, Malaysia, and the Philippines. The goal was to build an organization that would validate a candidates engineering fundamentals, prove their individuals skills, and enhance their networking ability. We wanted to do this in a way that was cost effective, time conscience, and utilized the latest technologies.

## MISSION

Based on engineering first principles and practical real world applications our curriculum has been vetted by academic and industry professionals. Through rigorous study and examination, candidates are able to prove their knowledge and experience. This body of certified professionals engineers will become a network of industry professionals leading continuous improvement and education with improved ethics.

## VISION

To become a globally recognized association for certification of professional engineers.

**WWW.IACPE.COM | INFO@IACPE.COM**

**KNOWLEDGE. CERTIFICATION. NETWORKING**

## LETTER FROM THE PRESIDENT

KARL KOLMETZ

### How to be Successful



Dear Friends,

There are thoughts on how to be successful. Here are a few of my personal beliefs.

**Maintain your health:** You will not be successful or wealthy without maintaining your health. Maintaining your health does not require major knowledge, but it is difficult to accomplish; eat healthy and exercise. For many people, both are hard to maintain.

**Have a long-term plan:** Successful people set long-term goals, and they know these aims are merely the result of short-term habits that they need to do everyday. Give up believing in the “Magic Bullet.” Overnight success is a myth. Successful people know that making small continual improvement every day will be compounded over time, and give them desirable results.

**Understand what is possible:** Nothing will ever be perfect, no matter how much we try. Fear of failure (or even fear of success) often prevents us from taking an action and putting our creation out there in the world. But a lot of opportunities will be lost if we wait for things to be right. Detach from the things you cannot control, focus on the ones you can, and know that sometimes the only thing you will be able to control is your attitude towards something. Remember, nobody can be frustrated while saying “Bubbles” in an angry voice.

**A smart fox only chases one rabbit:**

*“You will never reach your destination if you stop and throw stones at every dog that barks.”*  
—Winston S. Churchill

Successful people know this. That’s why they choose one thing and then beat it into submission. No matter what it is; a business idea, a conversation, or a workout. Being fully present and committed to one task is indispensable.

**Time Killers:** Impulsive web browsing, social media, television watching and gaming are the diseases of today’s society. These should never be an escape from your life or your goals. Unless your goals depend on either, you should minimize (or even eliminate) your dependency on them and direct that time towards things that can enrich your life.

All the best in your career and life,

Karl

# BECOME A CERTIFIED ENGINEER



IACPE supports engineers developing across emerging economies focusing on graduates connecting with industrial experts who can help further careers, attaining abilities recognized across the industry, and aligning knowledge to industry competency standards.

IACPE offers certification in the following engineering fields:  
Mechanical, Metallurgy, Chemical, Electrical, Civil, Industrial, Environmental, Mining, Architectural, Bio, Information, Machine and Transportation.

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# NEWS

## RECENT IACPE ACTIVITIES

IACPE President Karl Kolmetz presented Keys to Project Management at Untag Surabaya (17 Agustus 1945 University), Surabaya, East Java, Indonesia in May.

IACPE awarded four scholarships to: Mr. Eko Doni Bagawara CPE 1; Mr. Muhajir Maulana CPE EIT; Mr. Ilham Sarimbah CPE EIT; and Ms. Ganis Nahayu Riswenda CPE EIT.

Mr. Ir.Joko Santoso, MMT.,IAI, CPE II was the recipient of an Executive CPE Member Card.

CPE EIT certificates were awarded to Mr. Ilham Sarimbah CPE EIT and Mr. Muhajir Maulana CPE EIT.



# Distinguished Practicing Engineer

Each year IACPE recognizes the outstanding accomplishments of engineering education and engineering technology through the “Distinguished Practicing Engineer” awards program. By their commitment to their profession, desire to further the Association's Mission, and participation in civic and community affairs, IACPE award winners exemplify the best in engineering education and engineering technology.

This award salutes leaders in engineering for their dedication to their field and their commitment to advancing the human condition through great engineering achievement and/or through innovation in engineering education and technology. There are three divisions: Academic Division, Technology Division, Young Engineer and Student Divisions.

In this issue IACPE is proud to announce the top candidates from each division and in the October issue the 2017 group of awardees will be announced.

## ACADEMIC DIVISION

### *Architectural Engineering*

1. Dr.Ir.Retno Hastijanti, MT

### *Chemical Engineering*

1. Dr. Sivakumar Kumaresan, CPE
2. Rita Dwi Ratnani, ST., M.Eng
3. Ery Fatarina, ST.,MT.,IPM, CPE

### *Electrical Engineering*

1. Ir.drs.Muradi Suwargina, MT
2. Dr.Ir.Achmad Daengs GS.,SE.,MM.,CPPM.,CPE
3. Ir.M.Asqar W, MT
4. Ir.Achmad Junaedi, MT.,M.Sc

### *Environmental / Green Engineering*

- Ir. Dr. Dominic Foo, CPE

### *Industrial Engineering*

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2. Dr. Dwi Yuli Rakhmawati, ST.,Ph.D.,CPE
3. Rini Oktavera S.T, M.MT

### *Information Engineering*

1. Dr.Ir.Muaffaq A.Jani, M.Eng, CPE

### *Mechanical Engineering*

1. Dr.Prantasi Harmi Tjahjanti, S.Si.,MT
2. Ir. Masriel Djamales MBA.,MM.,CPE

## TECHNOLOGY DIVISION

### *Seperations*

1. Daniel Summers
2. Michael Resetarits

### *Heat Transfer*

1. Ir.Gatot Boedhi Tjahjono, MSME, MSIE
2. Shankar Chattopadhyay

### *Ethylene Technology*

1. Helmilus Moesa, CPE
2. Alex Micheal

### *Petrochemicals*

1. Tim Zygyula, CPE
2. Lee Pheng
3. Dr. Joseph Lim

### *Refining*

1. Andrew Sloley
2. Rick Cary

### *Mechanical Engineering*

1. Erebert Caracas
2. Hermis Kornelius

### *Chemical Engineering*

1. Supriyanto
2. Wiroon Tanthapanichakoon
3. Parthiban Siwayanan

### *Process Safety*

1. Stephen Wallace
2. Derrick Gradney

### *Information Technology*

1. Randy Conley PE PMP

### *Polymers*

1. Mohd Rohizat Abdul

## STUDENTS

### *Sekolah Tinggi Technology Fatahillah, Cilegon-Banten*

1. M.Salem Abdul Ajes, ST, CPE II
2. Maulana Ainul Yakin, ST.,CPE I
3. Muhammad Afra, CPE I

### *Institute Technology Indonesia, Tangerang, Banten*

1. Ruly Octora Suseno, ST.,CPE I
2. Choirul Anam, ST.,CPE I
3. Ade Sonjaya, CPE I

### *17 Agustus 1945 University, Semarang, Central Java*

1. Achika Augusti Ramanitya, CPE I
2. Muchamad Agus Purnomo, CPE I
3. Intan Ardyagarini Widyastuti

### *17 Agustus 1945 University, Surabaya, East Java*

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3. Meydin kartika Sari

### *Wahid Hasyim University, Semarang, Central Java*

1. ninik indah hartati
2. revy andar raesta
3. windi arum mukti

### *Serang Raya University, Serang, Banten*

1. Naimi, ST.,CPE I
2. Hery Purnama, ST., CPE I

### *Sultan Ageng Tirtayasa, Cilegon, Banten*

1. Mohamad Fajar Himatullah
2. Wahab Arrie Rachman
3. Khumaedi Muharom

# The Economic Advantage Added by Specialized Knowledge of Distillation Fundamentals

Karl Kolmetz CPE  
KLM Technology Group

## 1.0 Introduction

**Knowledge** is a familiarity with someone or something, which can include information, facts, descriptions, and/or skills acquired through experience or education. It can refer to the theoretical or practical understanding of a subject

**Wisdom** is a deep understanding of people, things, events or situations, resulting in the ability to choose or act to consistently produce the optimum results with a minimum of time, energy or thought. It is the ability to optimally apply perceptions and knowledge and so produce the desired results.

**The Law of Comparative Advantage** is the ability of an individual, company, or economy to conduct an activity better than another for some fixed and sometimes almost unchangeable reason. Comparative advantage is important in making decisions such as what products one should make or sell; if a company is unable to make a product as well as another and that is unlikely to change, the company might be well advised to make a different product.

**Kolmetz Law of Specialized Knowledge Advantage** is the ability of an individual, company, or economy to conduct an activity better than another, for a changeable reason such as specialized knowledge

## 2.0 Distillation Specialized Knowledge

In most chemical processing systems two main unit operations dominate; chemical reaction followed by separation. From the reactor, the reactants are then sent to a separation unit. In the separation unit, the reactants are separated into desired products, unreacted products for recycle, and unwanted or by products.

It has been estimated that the capital investment in separation equipment is 40-50% of the total for a conventional hydrocarbon processing unit. Of the total energy consumption of an average plant, the separation process accounts for about 50% to 70% of the energy consumption of the plant.

There are many separation processes and each one has its best application. They include distillation, crystallization, membrane, and fixed bed adsorption systems. Occasionally the best system may be a combination of these systems fundamentals.

The choice of the best application should be based on the life cycle cost. The life cycle cost is the initial capital cost of the plant along with the first ten years operating and maintenance cost. The life cycle cost should include a reliability factor, which is very important in designing any process plant equipment, reactors or separation equipment. Improved reliability has a very large impact on return on investment (ROI). Many life cycle cost only review energy, but not solvent, adsorbent, or catalyst cost because of accounting rules and this can lead to skewed economic decisions.

Distillation may be the most economical and utilized when possible. Distillation is the separation of key components by the difference in their relative volatility, or boiling points. It can also be called fractional distillation or fractionation. Distillation is favored over other separation techniques such as crystallization, membranes or fixed bed systems when;

1. The relative volatility is greater than 1.2,
2. Products are thermally stable,
3. Large rates are desired,
4. No extreme corrosion, precipitation or sedimentation issues are present,
5. No explosion issues are present

### 3.0 Extend Unit Run Length (Reduce Maintenance Cost)

Hydrocarbon Producers are exploring avenues to extend the on-stream time between outages for maintenance. Key equipment that can determine the end of run includes: catalyst life, cyclone erosion, and compressor and tower fouling. Critical equipment that has been shown to be a limiting factor can be duplicated to extend run length: for example, parallel pumps, reactors and reboilers.

This is a successful method to extend on-stream time, though it is expensive and in fact, at times cost prohibitive. Incorporating design guidelines that increase the on-stream time of the key pieces of equipment is a better economic decision for most plants.

Currently Refiners are planning four-year run lengths and Ethylene Producers are getting greater than five-year run lengths. These targets present challenges for distillation column design. Potential problem areas include refining vacuum wash oil beds, ethylene plant quench and saturator towers, and butadiene and other polymer producing distillation columns. Each of these applications has some common characteristics.

A review of successful and not so successful designs can help develop key design criteria. Design guidelines (best practices) developed from successful and not so successful applications can improve the on-stream time of each of the applications.

For distillation, the most significant non-capital component to the life cycle cost would be energy, followed by maintenance losses. To minimize energy, a designer should focus on column sequence and optimizing individual tower performance, as well as considering the impact of tray and packing efficiencies. The designer should also review the reliability of the equipment and scrutinize the complexity of the process to achieve minimal downtime for maintenance.

#### 3.1. The Correct Distillation Equipment for the Process Conditions

There are many types of processes that are grouped together and called distillation. Most have similarities, but some have noticeable differences. A partial list of the distillation grouping includes; (5)

1. Distillation
2. Absorption
3. Stripping
4. Extractive Distillation
5. Reactive Distillation
6. Azeotropic Distillation
7. Batch Distillation

There are several choices of distillation equipment for each of these operations. The choice of which to utilize depends on the 1) pressure, 2) fouling potential, 3) liquid to vapor density ratio, 4) liquid loading, and most important 5) life cycle cost. Distillation equipment includes many categories of equipment. The two major categories are trays and packing, but each of these categories has many divisions.



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Address : Ruko Golden Boulevard Blok K No. 1-2  
Jl. Pahlawan Seribu, BSD City, Serpong  
Tangerang 15322 – Indonesia  
Phone / Fax : +62 21 53150601  
Email : [info@ntp-eng.com](mailto:info@ntp-eng.com)

Tray divisions include;

1. Baffle Trays
2. Dual Flow Trays
3. Conventional Trays
4. High Capacity Trays
5. Multiple Downcomer Trays
6. System Limit Trays

Packing divisions include;

1. Grid Packing
2. Random Packing
3. Conventional Structured Packing
4. High Capacity Structured Packing

There are both process and economic arguments for the best choices in equipment selection. Typically, structured packing is better than random packing for fouling service because it has no horizontal surfaces, but if the process has high maintenance concerns, random packing may be chosen to reduce the life cycle cost.

#### Fouling Potential

Designing mass transfer equipment for fouling service requires first an understanding of the fouling mechanism, the process in which the fouling occurs, and behavior of the process when the fouling is present. An understanding of these items needs to be developed in advance of designing mass transfer equipment for fouling service.

The challenges of operating fouling columns can result in;

1. Increase energy consumption due to heat transfer and efficiency issues.
2. Reduced column capacity, which may lead to production losses.
3. Increased down time for cleaning and disposing of fouling wastes
4. Potential need for the use of chemical additives

#### Vapor to liquid density ratio

When structured packing was first introduced, the vapor to liquid density ratio was not understood, and structured packing was applied in areas of low vapor to liquid density with unexpected results. In one case an Alky Unit De Iso Butanizer was revamped from trays to rings with less performance, the original trays were then reinstalled. Several Propylene and Ethylene Splitters were revamped to structured packing, and then had trays re-installed.

Pressure normally has a large effect on the parameters of surface tension and density ratios. Density ratio is the ratio difference between the vapor and the liquid densities. Structured packing can be utilized if the density ratios are large. If the density ratio is below 50, a back-mixing effect can occur, where the liquid carries the vapor downward.

The resultant stage efficiency (HETP) in a packed column is lower than expected and trays may be the most economical solution. Both packed and trayed columns have reduced capacity factors as the pressure increases.

Trayed column are also affected by the vapor to liquid density ratio. The down comer capacity is directly affected by the ability of the liquid vapor mixture ability to separate into their respective phases. At low vapor to liquid density ratios this can be difficult if the down comers are not sized properly.

#### Liquid loading

In low liquid loaded systems packing may be the best choice because of the mass transfer characteristics of packing. The mass transfer in packing applications takes place on a thin film of liquid that is spread over the surface area of the packing. If the liquid rate is high this boundary layer will increase, reducing the mass transfer. Trays should be considered by high liquid loaded applications.

In low liquid loaded systems trays can have high residence times leading to undesired affects such as fouling, discoloration, polymerization, and sedimentation. In addition, trays in low liquid loaded systems have difficulty maintaining a good weir loading and distribution across the tray, resulting in lower than expected tray efficiencies.

### 3.2 Correct process control strategy to achieve stable operations

#### Pressure Control Challenges

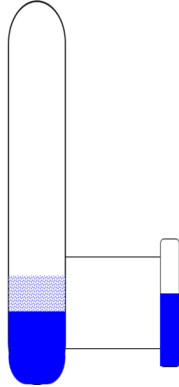
Because humans are less sensitive to pressure than temperature, we measure pressure in large units. In the ideal gas law  $PV = nRT$ , pressure is measured in units of 1 bar and temperature in units of degrees Kelvin, therefore temperature measures will be much more accurate than pressure measurements. Control strategies that rely strongly on pressure will be less stable than those that rely on temperature.

Of DeButanizer tower malfunctions, the most common malfunctions are widely different from those in vacuum, crude and FCC fractionators. Ten of the thirty-seven were in process control, and five of them were with pressure and condenser controls. The challenge of DeButanizer condenser is with the non-condensables that the previous towers might not totally remove.

#### Level Instrumentation Challenges

Level instrumentation is much more difficult than many people perceive. Acceptable industry standard methods have greater than 10% inaccuracy. This is due to density differences in the tower bottoms and the level leg or sight glass.

The tower bottoms will be frothy and at a higher temperature than the level leg. Because the principle of level measurement is Bernoulli's Equation (density times gravitational force times height) the density has a direct effect on the measurement. The density is a function of the temperature and the froth aeration, both of which are reduced in the sight glass and level leg. For a hot system the level in the tower can be as much as 10% higher, and for a cryogenic system the level can be lower than the sight glass due to the temperature effect.



Olefins Unit Application Example

An example of the phenomena by one of the authors was in an ethylene furnace steam drum. Because the steam drum has a low level shutdown, which also shut down the furnace, the operations group wanted to run the drum at a high liquid level to allow increased the operator response time. Operations decided to keep the drum level at 80%.

This drum operated at a 100 bar system pressure which has resulted in very high temperatures. Operations noted that there was a loss of efficiency in the steam turbines that utilized the high pressure steam. Tests were run to determine the carry over of the steam drums by measuring the sodium levels in the steam. It was determined by the sodium test, that the drums were full at 80% as verified by the photographs of the tide marks in the steam drums at the next down turn. The steam drum level was lowered to a measured 65% to reduce liquid carryover.

Picture of water mark on the steam drum



### Steam Turbine Fouling



### 3.3 Fouling / corrosion / polymerization potential

The most suitable mass transfer equipment for fouling service may also be the least efficient for mass transfer. Grid packing and shed decks can handle nearly every known fouling service, but they have low efficiencies when compared to sieve trays, random, and structured packings.

#### Packing

For packed towers the key fouling factors revolve around liquid distribution and packing residence time. The longer the residence times the less suitable. Low-pressure drop, smooth surface, low residence time packings perform best in fouling service. The order of preference is:

1. Grid
2. Structured packing
3. Random packing

#### Packing Distributor Concerns

In fouling service, distributors are areas where residence time is increased and fouling phenomena can occur. In high-fouling services trough v-notch or other type of trough distributors are recommended over pan type distributors.

#### Trays

The industry prefers trays in fouling service because of the long history of success trays have had in fouling service applications. The first continuous distillation column with bubble cap trays was developed in 1813 and structured packing was developed in 1964. The database and application know how is much larger with trays. The best trays to use in fouling services are dual flow trays and large fixed opening devices. Moveable valve trays are less resistant to fouling because the valves are areas where a polymer can seed and propagate. Solids can pack in small crevices around movable valves making them immovable.

## Dual Flow Trays

Dual flow trays are the trays of preference for heavy fouling services, but have low stage efficiency. Dual flow trays have no down comers, where products of fouling phenomena can accumulate. Stagnation in a down comer, or even on a tray deck, due to back mixing, can result in polymer formation.

The vapor and liquid transfers up and down the column thru the holes on the tray deck. This is an advantage if the fouling is in the vapor state as the under side of the tray is continually washed. The continuous agitation of the liquid on the topside of the trays combined with continuous underside wetting/washing action makes this tray suitable for fouling services. The challenge of the dual flow tray is mal-distribution in large diameter towers.

Two types of dual flow trays are available; standard deck and rippled deck. The standard deck has is a flat plate, and the rippled deck has sinusoidal waves. Levelness is of extreme importance to dual flow trays because the liquid will migrate to the low level on the tray and start channeling. Dual flow trays have a tendency for harmonic tray vibrations; rippled decks have an excellent record in fouling service except for one recent documented case.

## Fixed Opening Trays

If mass transfer efficiency and fouling resistance are both needed, then a fixed opening tray is the preferred choice. This fixed opening device is a raised opening on the tray deck that is sufficiently large to allow vapor to keep the tray deck non-fouled, while providing higher stage efficiency.

## 3.4 Thermal stability, chemical stability and safety

There are several incident of thermal stability, chemical stability and safety incidents that need review

### Thermal Stability

Thermal stability is an issue when dealing with many specialty chemicals. The need to reduce the tower bottoms temperature to reduce degradation or polymerization can shift the process design toward packing, falling film reboilers and special over head condensers to reduce the tower pressure drop.

### Chemical Stability

In several applications, a small amount of the feed stream can accumulate in a distillation column and have chemical stability issues. In an ethylene plant propylene splitter tower, Methyl Acetylene and Propadiene can concentrate in a section of the distillation tower below the feed.

At high concentrations, above 40%, this product can auto decompose resulting in large pressure increases with potential damage to the equipment.

In butadiene plants a small amount of vinyl acetylene is always present. Extractive distillation is typically used to recover the valuable 1, 3 butadiene. If not operated correctly, the vinyl acetylene can accumulate to an auto ignition level resulting in pressure vessel failure and consequential damages.

## Column Safety

One issue for column safety is packing fires. Packing has been known to ignite and burn when the tower is opened for maintenance. FRI and others have produced guidelines for reducing the likelihood of tower packing fires.

## 3.5 Maintenance reliability, accessibility and simplicity of repair

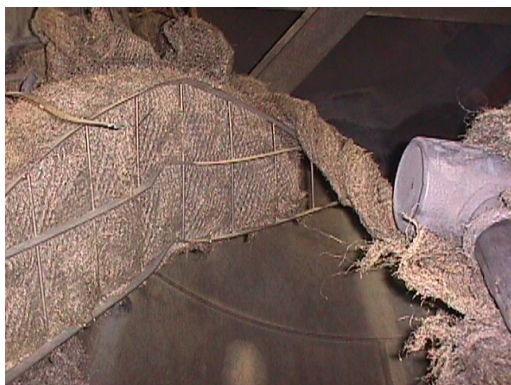
Maintenance reliability, accessibility and simplicity of repair issues many times are developed in actual field experiences. The field experience is fed back to the tray designer to incorporate best practices. This is an area where an experienced team can bring huge value to a process.

## Demister Pads

Demister pads are very easy to design and install, but tend to be high maintenance issue items. Typical entrainment removal of 99% can be obtained with 150 mm (6 inches) of mesh pads. There have been numerous failures in demister pad systems due to pressure surges. The pad may foul with material and fail due to pressure drop increases.

## Typical Demister Pad Issues





#### 4. Optimize Distillation Energy (Reduce Energy Cost)

For distillation the most significant non-capital component to the life cycle cost would be energy, followed by maintenance losses. To minimize energy, a designer should focus on column sequence and optimizing individual tower performance, as well as considering the impact of tray and packing efficiencies. The designer should also review the reliability of the equipment and scrutinize the complexity of the process to achieve minimal downtime for maintenance.

##### Stage Efficiency

Many things influence stage efficiency. The first and foremost is the type device employed for the service. Next is the system itself including the pressure, L/V ratio, relative volatility, and physical properties.

The choice of device is important from the viewpoint of capacity, but many times a higher capacity device will inherently have a lower level of efficiency performance. Generally, higher capacity devices exhibit lower efficiency. The reason for this is that the contact time between the liquid and the vapor is greatly reduced at higher throughput.

##### Design

##### Design of Trays to Improve Efficiencies and Capacities

Trayed Columns utilize a pressure and temperature differential to separate the products. For most trayed columns, the weir holds a certain amount of liquid level on each tray. The vapor must overcome this liquid head to move up the column. On the tray the vapor and liquid are contacted and then above the tray they are separated. Any deviation that restricts the vapor and liquid from contacting and then separating will deteriorate the column's ability to meet design specifications.

Items that lead to improvements in tray efficiency include;

1. Path flow length
2. Deck opening size
3. Elimination of stagnant zones
4. Down comer outlet devices / froth promoters
5. Weir Heights

##### 1. Path Flow Length

The longer the path flow length, the higher the tray efficiency. At short path flow lengths, less than 300 mm a tray will achieve the point efficiency. Longer flow path lengths can actually allow a tray to achieve efficiency in excess of 100%.

##### 2. Opening Size

There is an optimum bubble size, therefore an optimum opening size. Too small or too large can affect the size of the bubble, leading to loss of efficiency. Here is the normal trade off between capacity and efficiency.

##### 3. Elimination of stagnant zones

Parallel flow across a cordial surface can lead to stagnant areas. Liquid directional push valves can help eliminated the stagnant zones.

##### 4. Down comer outlet devices / froth promoters

The clear liquid exiting the down comer becomes froth on the tray. Items that assist this froth generation improve efficiency.

##### 5. Weir Heights

The weir height has an effect on the tray efficiency. Recommendations are not to exceed 100 mm or 1/6 of tray spacing, and 50 to 75 is suggested for all services except vacuum services.

##### Optimum Reflux Rates

Optimum reflux rates particularly for the cold refrigerated column can lead to very large energy savings. A cost of each reflux and reboiler energy needs to be calculated and incorporated in operations Key Performance Indicator.

## 9. Distillation Trouble Shooting

Even in the best run plants operations degrade over time or some processes do not work as well as expected. Plant operating and equipment changes introduce new problems and reveal, older, unappreciated problems.

Troubleshooting, the systematic investigation or problems and their solution, is key to maximizing plant profits. A unit with malfunctioning equipment or an incorrect process configuration cannot be optimized by the best control system available. Processes and equipment must work correctly for maximum profits.

Key aspects of successful troubleshooting include: a thorough understanding of both the process and the equipment; application of chemical engineering basics to problem solving; and good field technique and data interpretation skills. The process is not independent of the equipment.

The equipment works as part of a process. Both must be understood for effective troubleshooting. Chemical engineering basics are required for understanding both the equipment and the process.

Finally, field technique and data interpretation skills are needed to gather required information. Often, troubleshooting fails due to faulty, incomplete and misleading numbers.

## 10. Operations Training

The success of every company depends of each employee's understanding of the business's key components. Employee training and development will unlock the companies' profitability and reliability. When people, processes and technology work together as a team developing practical solutions, companies can maximize profitability and assets in a sustainable manner. With separation being typically over 40% of a plants cost and energy it is vital that your operation team understand distillation fundamentals.

The unit on stream time is an indication of operations training. A first quartile-operating unit's on stream factor is greater than 97%. If the on stream factor is below 97% a review of operation training and development is warranted. If on stream factor or average years of operating experience is declining a review of operations training and development should be considered.

A review of each trainer's experience and knowledge is critical when choosing an operations development program. Suppose the trainer understands 90% of the subject. At best, he might be able to teach the students 75% of his knowledge base on a short course basis. Therefore the student's knowledge base is 67%. If this person goes and trains someone else, the second student's knowledge base is 51%.

Make sure that you have qualified instructors with a high level of the subject understanding or your results will not be satisfactory. Be careful in "Train the Trainer" philosophy to get a high level of the subject knowledge to your trainer.

Operations training and development is an investment in the future - maximize your return on investment. Give your employees the keys to success.

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# How Many Pressure Relief Devices (PSDs) Do you Have Venting to Atmosphere? Are They Safe?

Process Engineering Associates



Determining if the atmospheric release from a pressure relief device (PSD) is safe is good engineering practice and a requirement defined by OSHA and ASME. Relief devices that are not connected to a closed relief system (flare header, knock out pot, etc.) should have tailpipes to direct the relieving stream to a safe area. An engineer can use readily available tools to preliminarily screen most atmospheric releases to determine if a more detailed quantitative evaluation is needed to generate a relief design guideline. The combination of preliminary screening, semi-quantitative evaluation and more detailed qualitative evaluation can be used to streamline the overall review process.

## Screening

Initial screening of each valve should be performed to categorize the level of risk. This involves a review of the existing PSD sizing calculations and existing hazards evaluation reports/recommendations to classify each device into one of the following categories based on the nature of the fluid discharged:

- Relief devices that simply need to be piped so that discharge does not have the potential to impinge personnel in its path or inhibit an operator from performing a function in an emergency. Example for this are low pressure steam releases or thermal cooling water reliefs.
- Relief devices that may have a slightly higher level of safety concern and will require some qualitative evaluation to define a specific relief guideline. Examples of this are release of an asphyxiant or saturated vapor that may condense.
- Relief devices that will require more detailed quantitative analysis to generate a relief guideline. Examples of this are flammable vapors, toxic vapors, vapors heavier than air, and vapors that may cause an offsite odor issue.
- Relief devices that are special cases. For example, a release that has been sized for vapor release but may have situations that could release a flammable liquid, a 2-phase mixture, or solids. These will require special design considerations.

Releases of liquids or solids to the atmosphere are not acceptable and will require special design (i.e. containment or safety instrumentation to eliminate a credible release scenario).

The screening step determines which valves should be carried further into a quantitative evaluation so that a relief guideline can be established. First and foremost, a conservative approach should be taken in the screening step to minimize the possibility that unsafe atmospheric PSD discharge could escape detection and not be flagged for further, more detailed, quantitative evaluation by the engineering team.

### **Semi-Quantitative Analysis**

Preliminary calculations are performed to compare data to key process parameters that allow for a more detailed definition of the potential risk associated with the release and determine if a more detailed quantitative evaluation (such as dispersion modeling) should be performed. The key variables include the following:

- *Adequate mixing* – API STD 521 6<sup>th</sup> edition 5.8 provides guidelines to determine if a relief device discharge to atmosphere is acceptable based on the mixing effects at the discharge. To semi-quantitatively determine if a release is acceptable, the following criteria must be met:

1. Exit velocity should be greater than 100 ft/sec. Studies have shown that the hazard of flammable concentrations existing below the point of discharge is negligible as long as the discharge velocity is sufficiently high. The evaluation should be done at various valve capacities (e.g. 25%, 50% and 100% of the rating) since there is a potential that the valve discharge rate may be lower than the actual rated capacity of the valve.

2. Vapor MW should be less than 80
3. Relief temperature should be at or below the atmospheric temperature.

If any of these criteria are not met, it should be assumed that adequate mixing may not exist and a potential for an unacceptable concentration at ground-level may be present.

- *Vapor density* – if the vapor density is heavier than air, the vapor cloud may migrate to ground level and pose a hazard. Additional analysis is needed to determine if the ground-level concentration could be flammable or toxic.
- *Vapor Reynolds Number (Nre)* – if the vapor Nre , per API STD 521 6<sup>th</sup> edition 5.8.2.2

$\rho_j$  = density of gas at the vent outlet

$\rho^\infty$  = density of the air.

then the jet momentum forces of release are usually dominant. Else, the jet entrainment of air is limited, and flammable mixtures can possibly occur at grade or downwind. Additional analysis is needed to determine if the ground-level concentration could be flammable or toxic.

Note: The above equation may not be valid for jet velocity < 40 ft/s (12m/s) or jet-wind velocity ratio < 10.

- *Potential for mist formation* - the potential for mist formation to occur exists if the relief stream dew point is above the minimum ambient temperature at the site. A design that includes a knockout drum or scrubber should be installed in relief lines to separate and remove liquid droplets from the discharge.
- *Maximum ground-level concentration (flammability and toxicity)* - a preliminary screening calculation to determine the maximum



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estimated concentration at grade ( $C_{max}$ ) can be done to determine if further dispersion modeling should be performed. This information can be compared to the lower explosive limit (LEL) for flammable vapors (is  $C_{max}$  greater than 25% of the LEL?) and to applicable exposure limits for toxic vapors (is  $C_{max}$  close to the IDLH or TLV for that compound?). For example, a highly flammable material released that is above the LEL at the release point should be evaluated for the potential to reach >25% of the LEL at grade.

Note: One reference that provides a screening equation for  $C_{max}$  is "Consequence Analysis of Atmospheric Discharge from Pressure Relief Devices, Qualitative and Quantitative Safety Screening" (Burgess, John P.E., Smith, Dustin P.E., Smith & Burgess Process Safety Consulting).

- Asphyxiant hazard – if an asphyxiant is discharged and the vapor release is heavier than air, additional evaluation may be needed, depending on the location of the relief device, to determine if there is a potential for buildup or re-entrainment of the vapors in occupied spaces.

Again, a conservative approach should be taken in the semi-quantitative analysis. Borderline acceptability of the above parameters should be considered for further modeling to ensure that the potential risk is accurately defined.

An example summary of the screening and preliminary semi-quantitative analysis is presented in the below summary table for a PSV releasing hexane.

PROCESS ENGINEERING ASSOCIATES, LLC SHEET 1 of 1 PRESSURE RELIEF DEVICE DISPOSAL TO ATMOSPHERE CALCULATIONS																																																							
Client:	Project No.:																																																						
Location:	PSV ID Number: PSV-XXX																																																						
Area / Unit:	Service: Hexane																																																						
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<b>RECOMMENDATIONS / COMMENTS:</b> 1) The vapor relief temperature exceeds the ambient temperature and may burn personnel in the area. 2) There is a potential to form mist that may settle to grade. 3) Built-up backpressure greater than 10% of set pressure. Recommend 4" diameter discharge pipe or replace PSV with a balanced bellows valve.																																																							

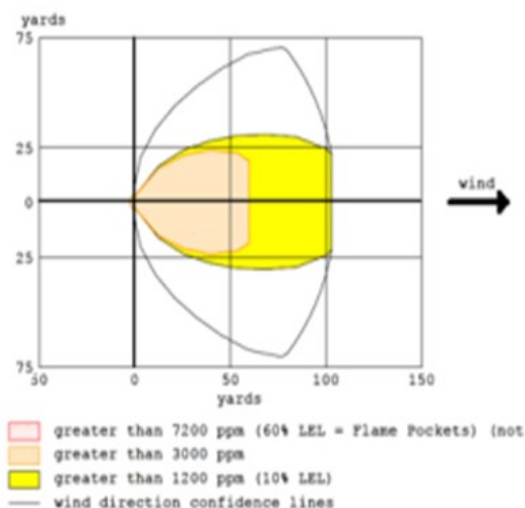
As a result of this semi-quantitative analysis, each valve can be classified into a specific risk category. Depending on the risks, you can either (1) define an atmospheric relief guideline for the valve so that the PSD design can be completed or (2) determine that a more detailed quantitative analysis (e.g. dispersion modeling) should be performed to better understand the potential risk.

### Detailed Quantitative Analysis

Results of the screening and preliminary semi-quantitative analysis may indicate that additional analysis (such as detailed dispersion modeling) is required to more specifically define the potential release pattern and level of risk associated with the vapor release such that a specific guideline can be established for the design of the tailpipe.

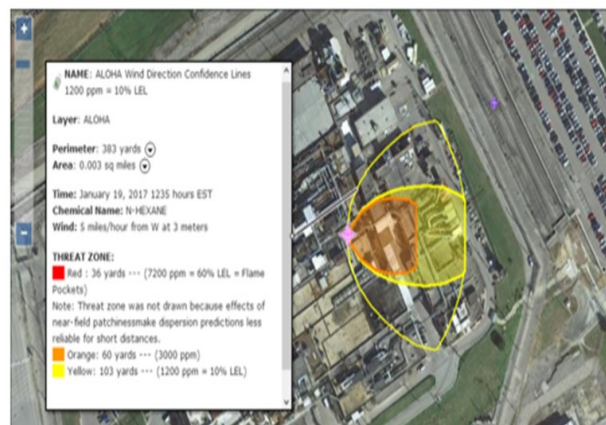
One method that is widely used to model these types of releases is ALOHA®. ALOHA® is a hazards modeling program that can define potential threat zones for chemical releases and can be used for flammable

vapors, toxic vapors, BLEVEs (boiling liquid expansion vapor explosions), jet fires, pool fires, and vapor cloud explosions. This software package is from the CAMEO® Software Suite and can be downloaded for free at <https://www.epa.gov/cameo>.



In the example above, ALOHA® was used to define the potential threat zones for the release of hexane from the PSD.

Using MARPLOT®, also a software program in the CAMEO Software Suite, the ALOHA threat zone estimate can be displayed on the map of the facility to graphically display the potential impact and better prepare for the chemical release.



### Conclusion

An engineer can use readily available tools to screen most atmospheric release PSDs to define a specific relief guideline for that PSD. The evaluation should include both a qualitative screening and, as needed, more detailed quantitative methods to streamline the review and develop documentation that proves the discharge configuration is safe.



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# Accurate Prediction of Phase Equilibrium Properties Using Peng Robinson Cubic Equation of State

Amit Katyal  
Independent Researcher/Inventor  
(Hydrocarbon and water treatment)  
Www.eq-comp.com

## Abstract

Phase equilibrium properties like bubble point, hydrocarbon dew point, water dew point, phase envelope, two phase composition, binary VLE curves, hydrate equilibrium curves etc. for hydrocarbon mixtures are required in all kinds of hydrocarbon handling. There is a need of accurately calculating these phase equilibrium properties using simple equations. In the present paper, accurate calculation of phase equilibrium properties of hydrocarbon mixtures using most simple to implement Peng Robinson cubic equation of state along with Van der Waals mixing rule is described. A phase equilibrium software, EQ-COMP, has been developed for this purpose and its features are also described in the paper.

## Theory

Present day hydrocarbon industry cannot function without accurate knowledge of phase equilibrium properties of pure hydrocarbons and hydrocarbon mixtures. Phase equilibrium properties of hydrocarbons are required in designing and effective operation of each and every equipment involving hydrocarbons ranging from hydrocarbon pumps to pressure vessels and distillation columns.

Phase equilibrium properties are also required in upstream hydrocarbon processes like planning and simulation of oil and gas wells and drilling and production of hydrocarbons. Atmospheres of various heavenly bodies in the universe are composed of hydrocarbons like methane, ethane, propane and heavier hydrocarbons in combination with inorganic gases like Nitrogen, Carbon dioxide and Hydrogen sulfide.

Exploration of these heavenly bodies require simulation of their atmospheres which require accurate prediction of phase equilibrium properties of the mixture of various hydrocarbons with inorganic gases constituting their atmospheres.

Bubble point, hydrocarbon dew point, water dew point, phase envelope, two phase composition, compressibility factors, binary VLE curves, hydrate equilibrium curve etc. are few of the phase equilibrium properties having wide applications in hydrocarbon handling. For calculation of simple phase equilibrium properties for ideal hydrocarbon mixtures at low temperatures and pressures, Raoult's law can be used. As per Raoult's law :  $Y_i = X_i \cdot P_i^o / P$

Where

$Y_i$  is mole fraction of  $i$  component in vapor phase

$X_i$  is mole fraction of  $i$  component in liquid phase

$P_i^o$  is vapor pressure of  $i$  component at system temperature in pure form, and

$P$  is system pressure

However, at high temperatures and pressures, even mixtures of simple hydrocarbon molecules deviate from ideality. For non-ideal hydrocarbon mixtures, fugacity coefficient based models for prediction of phase equilibrium properties are used. The fugacity of a real gas is the effective partial pressure of a component which replaces ideal partial pressure of the component in calculation of distribution of the component in liquid and vapor phase. The ideal gas pressure and fugacity are related through a dimensionless fugacity coefficient

$$\Phi = f/P$$

Where  $\Phi$  is fugacity coefficient

$f$  is fugacity

$P$  is ideal gas pressure

For a condensed phase (liquid or solid) in equilibrium with its vapor phase, fugacity of its components is equal to their fugacity in vapor phase. Fugacity of non-polar or mildly polar compounds can be calculated to reasonable accuracy using equations of state. Hydrocarbons and inorganic gases present in oil and natural gas mixtures are non-polar or mildly polar in nature. As equations of state require very few parameters like critical pressures, critical temperatures and acentric factors and can be used to calculate both liquid and vapor phase fugacity so these are widely used in phase equilibrium calculations of hydrocarbon mixtures in petroleum industry.

Numerous equations of state are given in literature. Out of these, Soave Redlich Kwong cubic equation of state and Peng Robinson cubic equation of state are most widely used. Generally Peng Robinson cubic equation of state is preferred over Soave Redlich Kwong cubic equation of state as it predicts liquid density more accurately.

The Peng–Robinson equation was developed in 1976 at The University of Alberta by Ding-Yu Peng and Donald Robinson. The Peng-Robinson cubic equation of state is given below:

$$p = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m^2 + 2bV_m - b^2}$$

$$a = \frac{0.45724 R^2 T_c^2}{p_c}$$

$$b = \frac{0.07780 R T_c}{p_c}$$

$$\alpha = \left(1 + \left(0.37464 + 1.54226\omega - 0.26992\omega^2\right)(1 - T_r^{0.5})\right)^2$$

$$T_r = \frac{T}{T_c}$$

In polynomial form:

$$A = \frac{a\alpha p}{R^2 T^2}$$

$$B = \frac{bp}{RT}$$

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0$$

Where,  $\omega$  is the acentric factor of the species and  $R$  is the universal gas constant.

For calculations involving hydrocarbon mixtures various types of mixing rules can be used. Van der Waals mixing rule is the simplest mixing rule used in Peng Robinson equation requiring minimum number of parameters. Van der Waals mixing rule is applied for mixtures and mixture parameters are calculated as given below

$$a = \sum_i^n \sum_j^n x_i x_j a_i^{0.5} a_j^{0.5} (1 - k_{ij})$$

$$b = \sum_i^n x_i b_i$$

Where:

$a$  and  $b$  = the interaction energy and molecular size parameters for the mixture

$a_i, b_i$  =  $a$  and  $b$  parameters for component  $i$  in the mixture

$x_i$  = composition (mole fraction) for component  $i$  in the mixture

$k_{ij}$  = binary interaction parameter

$n$  = number of components in the mixture

Binary interaction parameters for groups of components can be calculated experimentally. However various correlations are also available to calculate binary interaction parameters. A common correlation to estimate the binary interaction parameter is given below:

$$k_{ij} = 1 - \left[ \frac{2 \sqrt{v_{c_i}^{1/3} v_{c_j}^{1/3}}}{v_{c_i}^{1/3} + v_{c_j}^{1/3}} \right]^n$$

In the above equation,  $v_{ci}$  and  $v_{cj}$  represent the critical volumes of components  $i$  and  $j$ , respectively.

The default value of exponent  $n$  is normally set to 1.2 but it can be used as a tuning parameter to match the experimentally measured dew point.

Temperature dependent binary interaction parameters can also be used in Van der Waals mixing rule. Temperature dependent binary interaction parameters give more accurate values compared to constant parameters or when no parameters are used.

E-Predictive Peng Robinson 78 (E-PPR 78) equation gives a correlation to calculate predictive values of temperature dependent binary interaction parameters. E-PPR 78 equation can give temperature dependent binary interaction parameters for mixtures containing water besides paraffins, cycloparaffins, olefins, di-olefins, aromatics, thiols and inorganic gases like nitrogen, carbon dioxide, hydrogen sulfide, hydrogen, argon and oxygen.

As E-PPR 78 equation can include water as a component so it can be used to calculate water dew point curves and hydrate equilibrium curves for hydrocarbon mixtures containing water accurately. Temperature dependent binary interaction parameters as per E-PPR 78 equation can be calculated using group contribution method using the following equation.

$$k_{ij}(T) = \frac{-\frac{1}{2} \left[ \sum_{k=1}^{N_i} \sum_{l=1}^{N_j} (a_{ik} - a_{jk})(a_{il} - a_{jl}) A_{kl} \times \left( \frac{298.15}{T/K} \right)^{\left( \frac{a_{kl}}{a_{ij}} - 1 \right)} \right] - \left( \frac{\sqrt{a_i(T)}}{b_i} - \frac{\sqrt{a_j(T)}}{b_j} \right)^2}{2 \frac{\sqrt{a_i(T) a_j(T)}}{b_i b_j}}$$

Where,  $a_{ik}$  is the fraction of molecule  $i$  occupied by group  $k$  (occurrence of group  $k$  in molecule  $i$  divided by the total number of groups present in molecule  $i$ ).  $A_{kl} = A_{lk}$  and  $B_{kl} = B_{lk}$  (where  $k$  and  $l$  are two different groups) are constant parameters given in **Appendix A** ( $A_{kk} = B_{kk} = 0$ ).

Accurate prediction of Vapor-Liquid Equilibrium properties requires complex calculations which can only be executed through complex computer programs run on latest computers.

EQ-COMP is a complex chemical engineering process simulation software tool for automatically calculating vapor-liquid equilibrium properties of pure hydrocarbons and binary and multi-component mixtures of hydrocarbons by just clicking a button. EQ-COMP can predict vapor-liquid equilibrium properties for hydrocarbon mixtures for almost any composition with up to a maximum of 112 components using Peng-Robinson cubic equation of state. Please visit [www.eq-comp.com](http://www.eq-comp.com) for complete information.

The possible components can include non-polar hydrocarbons, mildly polar hydrocarbons, non-polar inorganic gases or mildly polar inorganic gases. Various modules of EQ-COMP can be used to find out bubble point temperature, bubble point pressure, hydrocarbon dew point temperature, hydrocarbon dew point pressure, phase envelope, two phase composition and compressibility factor. EQ-COMP can accurately predict VLE properties in retrograde region and for compositions involving high proportions of non-condensates.

The phase envelope generated using EQ-COMP consists of equilibrium temperature values at a specified interval of 0.4 bars. This phase envelope clearly marks the critical point of mixture and cricondenbar and cricondentherm for the mixture can also be located on the phase envelope.

Carbon dioxide freezing and frost curve for hydrocarbon mixtures containing CO<sub>2</sub> can be calculated using EQ-COMP. Carbon dioxide freezing and frost curve is calculated by using temperature dependent binary interaction parameters (BIPs) in Peng-Robinson cubic equation of state. This curve provides safe operating temperature and pressure conditions for handling hydrocarbon mixtures containing CO<sub>2</sub> under cryogenic conditions.

Separate modules are designed to find out water dew point curve for mixtures containing water between 1 weight % and 50 weight % and gas hydrate equilibrium curve for hydrocarbon mixtures using temperature dependent binary interaction parameters (BIPs) in Peng Robinson equation.

Gas hydrate dissociation curve / gas hydrate equilibrium curve for pure hydrate forming components and hydrocarbon mixtures containing at least one hydrate forming component can be calculated using EQ-COMP. Hydrate forming components included in EQ-COMP are methane, ethane, propane, n-butane, i-butane, ethylene, propylene, cyclopropane, nitrogen, hydrogen sulfide, carbon dioxide, argon and oxygen. Also hydrate equilibrium curves for pure hydrocarbons and hydrocarbon mixtures in presence of hydrate inhibitors like salts (LiCl, NaCl, KCl, CsCl, CaCl<sub>2</sub> and MgCl<sub>2</sub>), salt mixtures, organic liquids (methanol, ethylene glycol, ethanol, 1-propanol, 2-propanol, t-butyl alcohol and glycerol), sugars (deoxyribose, ribose, fructose, sucrose, glucose and maltose), urea and formamide can be calculated using EQ-COMP.

Concentration diagrams (x-y plot), temperature concentration diagrams (T-x-y plot) and enthalpy concentration diagrams (H-x-y plot) can be generated for binary mixtures using binary VLE calculation module of EQ-COMP. These diagrams can be used in McCabe Thiele method and Ponchon Savarit method to design distillation columns for binary hydrocarbon mixtures.

More accurate basic stage by stage design calculations for binary distillation columns and multicomponent distillation columns to find out minimum reflux ratio, number of equilibrium stages in rectification section and stripping section, equilibrium temperature of various stages and liquid and vapor compositions at various stages can be performed using multicomponent distillation calculation module of EQ-COMP.

Also various thermodynamic properties for hydrocarbon mixtures like enthalpy, entropy, Gibbs free energy, specific heats and sonic speed can be calculated using thermodynamic properties calculation module of EQ-COMP.

Up to a maximum of 40 Pseudo components can be included in various VLE calculations using EQ-COMP.

EQ-COMP software uses modified version of Peng-Robinson cubic equation of state given in 1978. Apart from the constant values of binary interaction parameters derived using critical volumes of interacting components given above, EQ-COMP can include any other binary interaction parameters in its calculations in case the same are provided by the user. EQ-COMP can also include temperature dependent binary interaction parameters as per E-Predictive Peng Robinson 78 (E-PPR 78) equation in its calculations. These parameters are supposed to increase the accuracy of prediction of VLE properties over constant parameters or no use of parameters. Temperature dependent binary interaction parameters are used in EQ-COMP to calculate water dew point temperature values where it provides accurate results comparable to CPA (cubic plus association) equation of state. Further EQ-COMP uses statistical thermodynamic model for clathrates developed by Van der Waals and Platteeuw in 1959 to predict hydrate dissociation curve for hydrocarbon mixtures.

Some of the graphical results of EQ-COMP are given in **Appendix B**.

## **Conclusions**

Phase equilibrium properties of hydrocarbon mixtures can be calculated very accurately using Peng Robinson cubic equation of state and Van der Waals mixing rule with constant and temperature dependent binary interaction parameters. EQ-COMP VLE software can be used for this purpose through [www.eq-comp.com](http://www.eq-comp.com) website.

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APPENDIX A

(Alk and Blk values are given in bars)

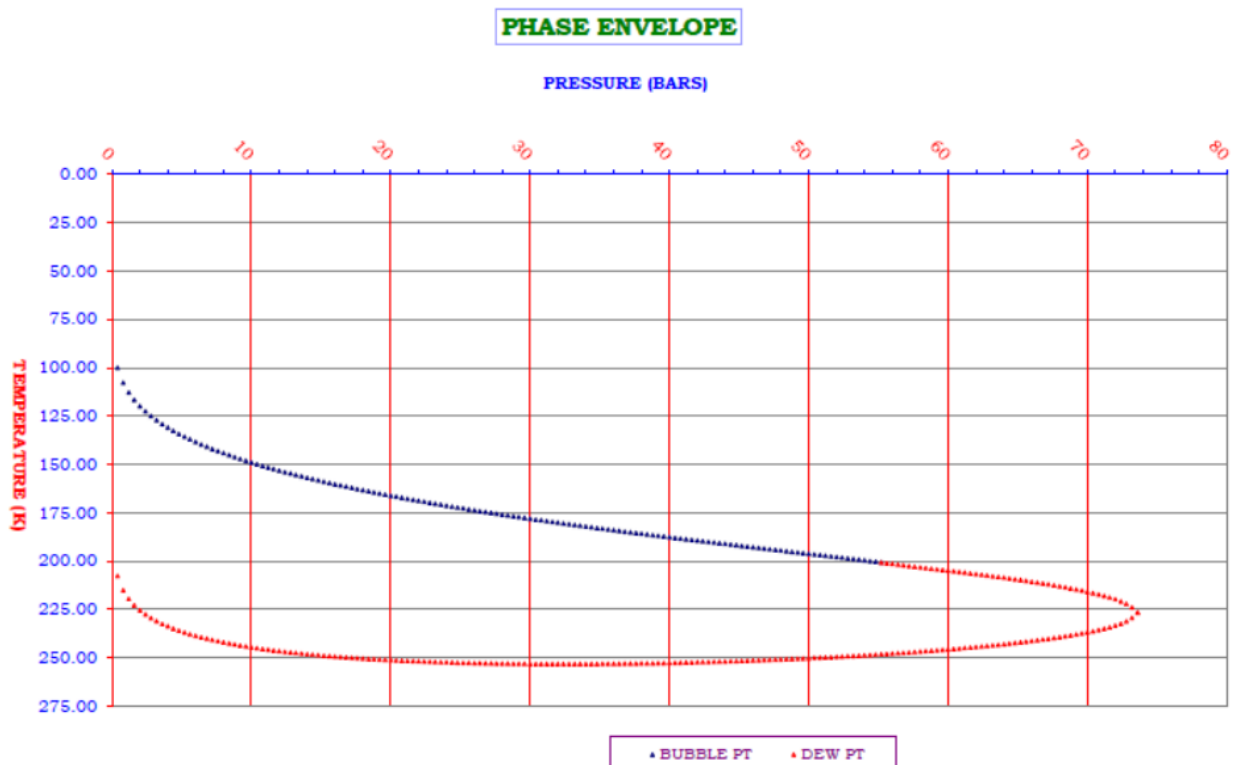
Alk	CH3	CH2	CH	C	CH4	C2H6	CH aro	Caro	Cfused aro	CH2cyclic	N2	CO2	H2S	H2O	H2	C2H4	CH2alkalke or Chalke	Calke	CH cycled or Ccycled	
	CH3	CH2	CH	C	CH4	C2H6	CH aro	Caro	Cfused aro	CH2cyclic	N2	CO2	H2S	H2O	H2	C2H4	CH2alkalke or Chalke	Calke	CH cycled or Ccycled	
CH3	0	655.4	2149.1	4315.7	284.8	37.7	988.3	1036.3	6248.7	435.8	2933.9	380.9	1448.1	1595.6	35573.9	1739.7	78.9	487.3	1026	470.1
CH2	655.4	0	390.5	1344.8	377.5	298.5	250.5	51.5	-178.4	85.8	634.8	837.3	1413.8	1365.7	43243.2	1554.5	597.1	0	648.5	343.1
CH	2149.1	390.5	0	-861.3	1314.2	1561.3	566.2	487.3	0	730.9	-1207.9	3836.4	1918.2	1925	9714.5	4152.1	1479	847.6	916.2	0
C	4315.7	1344.8	-861.3	0	3095.2	3881	1705.4	1283.4	0	2086.3	250.5	3417.7	3774.6	3307.9	0	2264.8	3668.2	1811.8	0	0
CH4	284.8	377.5	1314.2	3095.2	0	99.5	672.6	1067.2	2491.2	339.7	1880.4	308.8	1348.6	1818.7	22647.6	1561.3	192.2	487.3	0	0
C2H6	37.7	298.5	1561.3	3881	99.5	0	411.8	679.4	0	127	1180.4	615.91	1362.3	1571.95	23333.9	1376	75.5	267.7	0	0
CH aro	988.3	250.5	566.2	1705.4	672.6	411.8	0	-164.7	525	288.2	1290.2	4907	984.8	212.8	22675.1	2848.1	257.4	99.5	-164.7	37.7
Caro	1036.3	51.5	487.3	1283.4	1067.2	679.4	-164.7	0	-3280.5	374	-991.7	3438.3	1544.2	96.1	5435.4	3774.6	978	-483.8	3431.5	2429.5
Cfused aro	6248.7	-178.4	0	0	2491.2	0	525	-3280.5	0	1406.9	-991.7	7024.2	3311.4	96.1	13403.2	5490.3	2096.6	6698.2	0	0
CH2cyclic	435.8	85.8	730.9	2086.3	339.7	127	288.2	374	1406.9	0	1389.7	1794.65	1441.2	1173.6	42107.4	2319.7	353.4	-154.4	1595.6	319.1
CH cyclic	2933.9	634.8	-1207.9	250.5	1880.4	1180.4	1290.2	-991.7	-991.7	1389.7	0	3314.8	2161.8	713.7	2439.8	-3139.8	2971.6	2601	0	1513.3
N2	380.9	837.3	3836.4	3417.7	308.8	615.91	4907	3438.3	7024.2	1794.65	3314.8	0	950.5	3194.69	25735.9	652	453	597.1	5414.8	0
CO2	1448.1	1413.8	1918.2	3774.6	1348.6	1362.3	984.8	1544.2	3311.4	1441.2	2161.8	950.5	0	1348.56	5593.3	2659.4	730.9	607.4	748.1	878.5
H2S	1595.6	1365.7	1925	3307.9	1818.7	1571.95	212.8	96.1	96.1	1173.6	713.7	3194.69	1348.56	0	60.394	1458.4	0	0	0	0
H2O	35573.9	43243.2	9714.5	0	22647.6	23333.9	22675.1	5435.4	13403.2	42107.4	2439.8	25735.9	5593.3	60.394	0	8307.6	16501.9	22434.9	0	0
H2	1739.7	1554.5	4152.1	2264.8	1561.3	1376	2848.1	3774.6	5490.3	2319.7	-3139.8	652	2659.4	1458.4	8307.6	0	1513.3	1629.9	6300.2	4831.5
C2H4	78.9	597.1	1479	3668.2	192.2	75.5	257.4	978	2096.6	353.4	2971.6	453	730.9	0	16501.9	1513.3	0	147.6	-5181.5	-988.3
CH2alkalke or Chalke	487.3	0	847.6	1811.8	487.3	267.7	99.5	-483.8	6698.2	-154.4	2601	597.1	607.4	0	22434.9	1629.9	147.6	0	247.1	140.7
Calke	1026	648.5	916.2	0	0	0	-164.7	3431.5	0	1595.6	0	5414.8	748.1	0	0	6300.2	-5181.5	247.1	0	236.8
Chcycalke or Ccycalke	470.1	343.1	0	0	0	0	37.7	2429.5	0	319.1	1513.3	878.5	0	0	0	4831.5	-988.3	140.7	236.8	0

Blk	CH3	CH2	CH	C	CH4	C2H6	CH aro	Caro	Cfused aro	CH2cycl ic	`CH cycl ic	N2	CO2	H2S	H2O	H2	C2H4	CH2alke or CHalke	Calke	CH cyalke or Ccycalke
CH3	0	1056.9	2948.7	5750.4	202.5	89.2	1362.3	1036.3	7741.4	600.5	1708.9	881.9	4014.8	2778.5	111948	2395.2	350	442.7	2601	1695.1
CH2	1056.9	0	415.9	1839.3	748.1	658.8	645.1	-75.5	-41.2	277.9	-744.6	1887.3	2371.1	1245.6	121261	2408.9	823.5	0	518.2	511.3
CH	2948.7	415.9	0	851	1575	967.7	1297.1	-892.2	0	713.7	185.3	3754	3808.9	5627.6	5675.6	7264.4	-555.9	1931.9	549	0
C	5750.4	1839.3	851	0	356.9	-2247.6	2841.2	1890.7	0	2944.2	813.3	6351.6	1626.5	-2971.6	0	18125	-2192.7	4189.8	0	0
CH4	202.5	748.1	1575	356.9	0	137.3	1674.6	1907.9	4083.4	54.9	4738.8	370.6	2192.7	3040.3	47216.9	929.9	332.9	682.9	0	0
C2H6	89.2	658.8	967.7	-2247.6	137.3	0	507.9	2106.9	0	280.293	-2127.5	849.22	2357.4	2170.74	51471.9	1499.5	209.3	-51.5	0	0
CH aro	1362.3	645.1	1297.1	2841.2	1674.6	507.9	164.7	2511.8	5692.8	535.3	367.2	4907	2535.8	61.8	62184.9	1750	789.2	199	614.2	17.2
Caro	1036.3	-75.5	-892.2	1890.7	1907.9	2106.9	164.7	0	-5692.8	535.3	-1935.3	6876.6	3743.7	-367.2	4117.7	12010.1	679.4	277.9	8801.7	-72.1
Cfused aro	7741.4	-41.2	0	0	4083.4	0	2511.8	-5692.8	0	2776	-1935.3	18886.7	2765.8	-367.2	-658.84	14755.3	38188.7	5895.2	0	0
CH2cycl ic	600.5	277.9	713.7	2944.2	54.9	280.293	655.4	535.3	2776	0	356.9	4045.2	3541.3	1664.3	130313	1674.6	525	243.6	1406.9	693.2
CH cycl ic	1708.9	-744.6	185.3	813.3	4738.8	-2127.5	367.2	-1935.3	-1935.3	356.9	0	3893.1	-1328	-1276.5	-603.94	-2257.9	-6471.7	1348.6	0	27.5
N2	881.9	1887.3	3754	6351.6	370.6	849.22	4907	6876.6	18886.7	2765.8	3893.1	0	2556.4	5500.63	54903.3	701	926.5	1345.88	947.1	0
CO2	4014.8	2371.1	3808.9	1626.5	2192.7	2357.4	2535.8	3743.7	2765.8	3541.3	-1328	2556.4	0	2014.27	2779.5	2683.4	1067.2	1839.3	-2666.2	669.1
H2S	2778.5	1245.6	5627.6	-2971.6	3040.3	2170.74	61.8	-367.2	-367.2	1664.3	-1276.5	5500.63	2014.27	0	59.913	8235.5	0	0	0	0
H2O	111948	121261	5675.6	0	47216.9	51471.9	62184.9	4117.7	-658.84	130313	-603.94	54903.3	2779.5	59.913	0	-1379.4	16608.3	51993.4	0	0
H2	2395.2	2408.9	7264.4	18125	929.9	1499.5	1750	12010.1	14755.3	1674.6	-2257.9	701	2683.4	8235.5	-1379.4	0	1650.5	3222.1	5730.5	24167.8
C2H4	350	823.5	-555.9	-2192.7	332.9	209.3	789.2	679.4	38188.7	525	-6471.7	926.5	1067.2	0	16608.3	1650.5	0	113.2	68148.7	18094.1
CH2alke or Chalke	442.7	0	1931.9	4189.8	682.9	-51.5	199	277.9	5895.2	243.6	1348.6	1067.2	1839.3	0	51993.4	3222.1	113.2	0	1218.2	-123.5
Calke	2601	518.2	549	0	0	0	614.2	8801.7	0	1406.9	0	947.1	-2666.2	0	0	5730.5	68148.7	1218.2	0	875
Chcycalke or Ccycalke	1695.1	511.3	0	0	0	0	17.2	-72.1	0	693.2	27.5	0	669.1	0	0	24167.8	18094.1	-123.5	875	0

# APPENDIX B

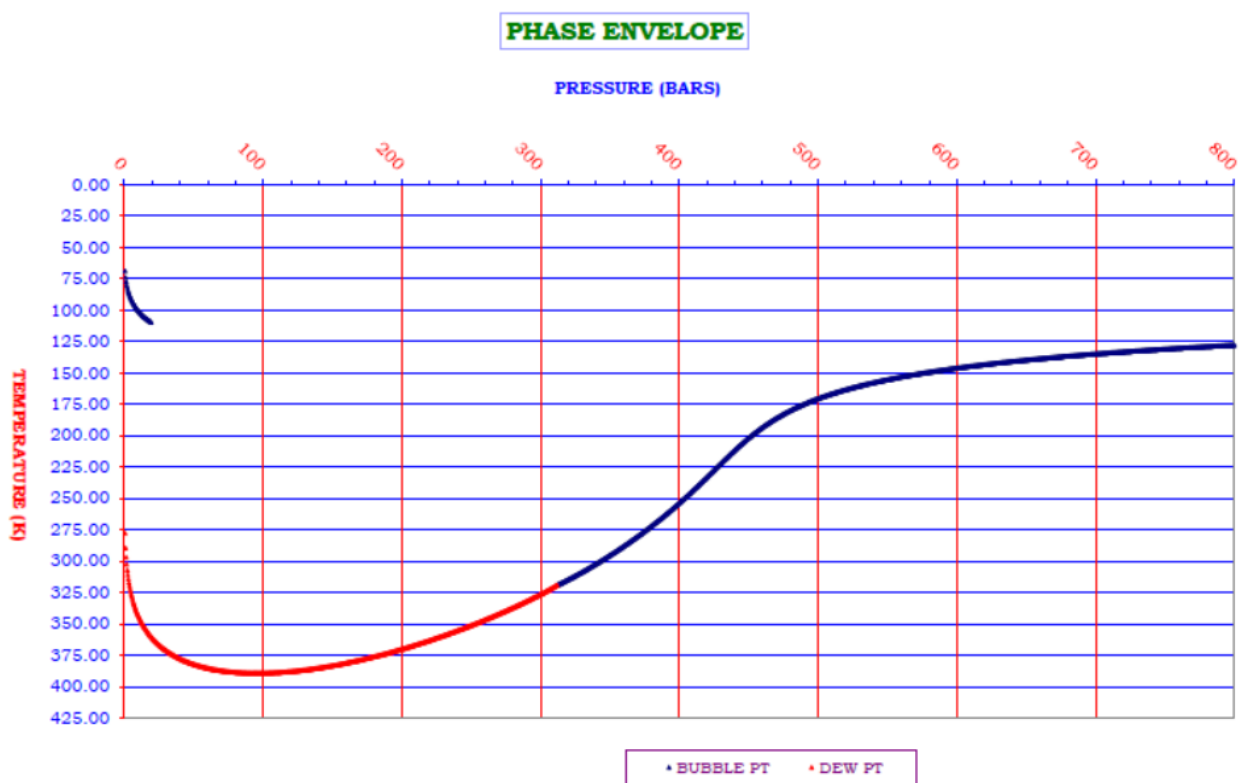
Phase envelope of a typical natural gas composition using EQ-COMP software

Components	Z
<b>Methane (CH<sub>4</sub>)</b>	0.958
<b>Ethane (C<sub>2</sub>H<sub>6</sub>)</b>	0.022
<b>Propane (C<sub>3</sub>H<sub>8</sub>)</b>	0.005
<b>Iso butane (C<sub>4</sub>H<sub>10</sub>)</b>	0.002
<b>n butane (C<sub>4</sub>H<sub>10</sub>)</b>	0.001
<b>n pentane (C<sub>5</sub>H<sub>12</sub>)</b>	0.000
<b>2-methyl butane (C<sub>5</sub>H<sub>12</sub>)</b>	0.001
<b>n hexane (C<sub>6</sub>H<sub>14</sub>)</b>	0.001
<b>Nitrogen (N<sub>2</sub>)</b>	0.006
<b>Carbondioxide (CO<sub>2</sub>)</b>	0.005
	1.000



**Phase envelop result for a hydrocarbon mixture with high proportion of non-condensables using EQ-COMP software**

Components	Z
<b>Ethane (C<sub>2</sub>H<sub>6</sub>)</b>	0.040
<b>Propane (C<sub>3</sub>H<sub>8</sub>)</b>	0.130
<b>Iso butane (C<sub>4</sub>H<sub>10</sub>)</b>	0.090
<b>n butane (C<sub>4</sub>H<sub>10</sub>)</b>	0.010
<b>n pentane (C<sub>5</sub>H<sub>12</sub>)</b>	0.040
<b>n hexane (C<sub>6</sub>H<sub>14</sub>)</b>	0.010
<b>n heptane (C<sub>7</sub>H<sub>16</sub>)</b>	0.010
<b>n octane (C<sub>8</sub>H<sub>18</sub>)</b>	0.010
<b>Nitrogen (N<sub>2</sub>)</b>	0.660
	1.000



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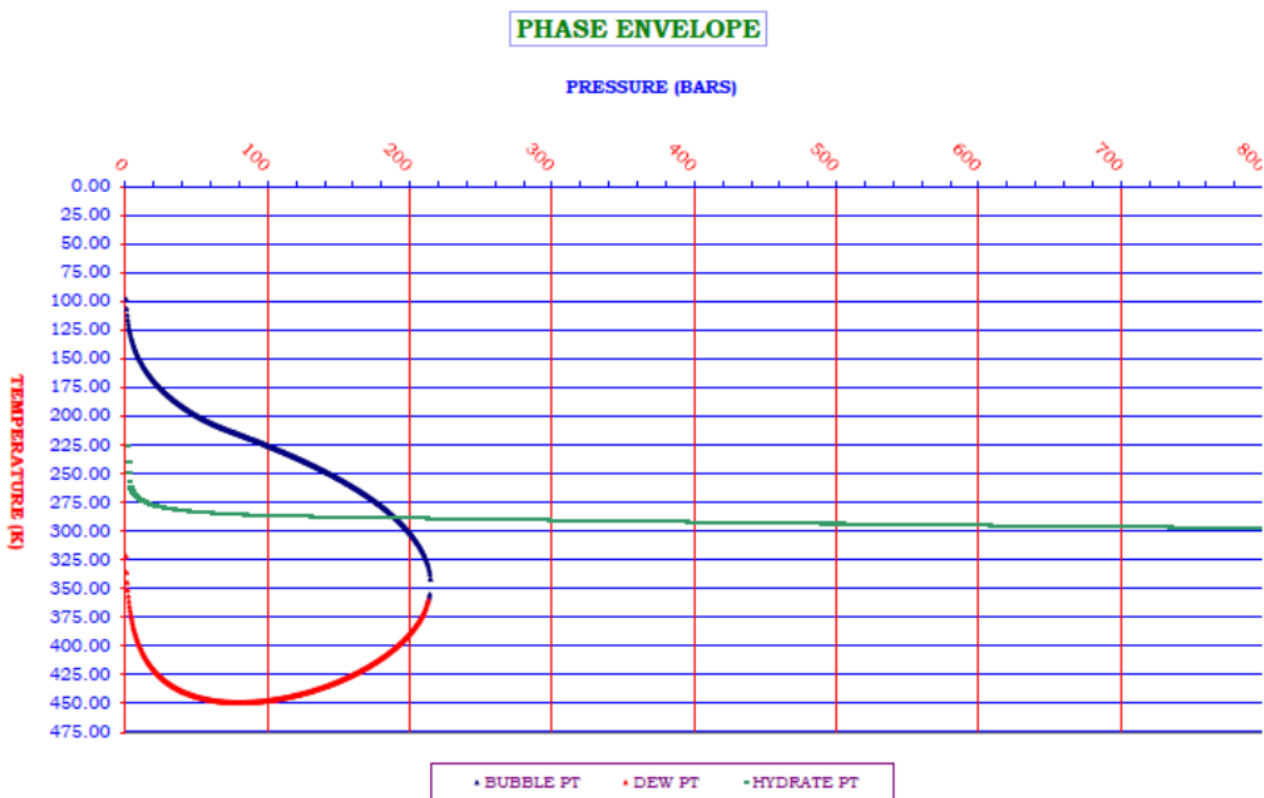
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### Hydrate equilibrium curve for Natural Gas composition

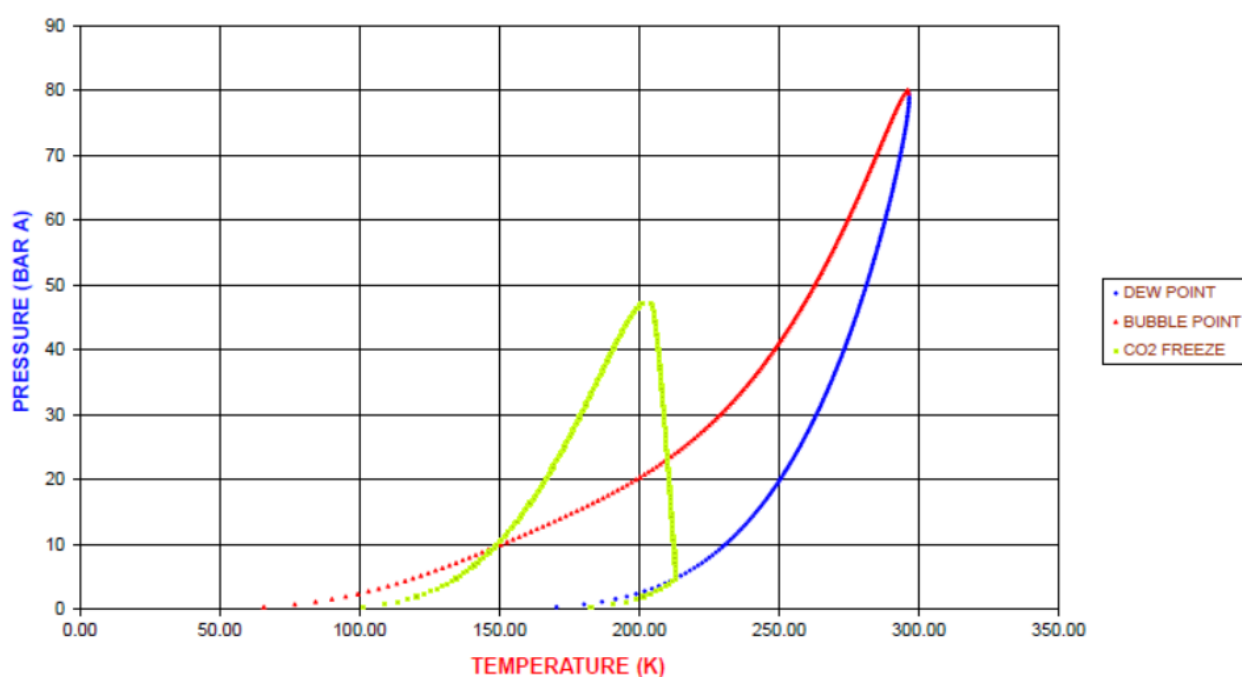
Components	Z
Methane (CH <sub>4</sub> )	0.650
Ethane (C <sub>2</sub> H <sub>6</sub> )	0.100
Propane (C <sub>3</sub> H <sub>8</sub> )	0.050
Iso butane (C <sub>4</sub> H <sub>10</sub> )	0.020
n butane (C <sub>4</sub> H <sub>10</sub> )	0.010
n pentane (C <sub>5</sub> H <sub>12</sub> )	0.020
n hexane (C <sub>6</sub> H <sub>14</sub> )	0.020
n heptane (C <sub>7</sub> H <sub>16</sub> )	0.020
n octane (C <sub>8</sub> H <sub>18</sub> )	0.020
n nonane (C <sub>9</sub> H <sub>20</sub> )	0.020
n decane (C <sub>10</sub> H <sub>22</sub> )	0.010
Benzene (C <sub>6</sub> H <sub>6</sub> )	0.020
Toluene (C <sub>7</sub> H <sub>8</sub> )	0.010
Nitrogen (N <sub>2</sub> )	0.010
Carbondioxide (CO <sub>2</sub> )	0.010
Hydrogensulfide (H <sub>2</sub> S)	0.010
	1.000



### Phase envelope with CO<sub>2</sub> frost and freezing curve using EQ-COMP software

Components	Z
Methane (CH <sub>4</sub> )	0.100
Carbondioxide (CO <sub>2</sub> )	0.900
	1.000

#### PHASE ENVELOPE WITH CO<sub>2</sub> FREEZING



### Biography



Mr. Amit Katyal is an independent researcher/ inventor based in New Delhi, INDIA. Mr. Amit Katyal is a Bachelor in Chemical Engineering from the Indian Institute of Technology, Delhi, INDIA and has a total experience of more than 20 years in hydrocarbon and water treatment sector in diverse segments like research, operations and technical services. Mr. Amit Katyal has developed some very useful softwares for hydrocarbon sector like EQ-COMP, HYD-PREDIC, LIQ-PROP, BUBBLE-SIM and MIX-CP. Additionally, Mr. Amit Katyal has also invented three patented/ patent pending technologies. One of the technologies gives usage of gas hydrate concept to desalinate high salinity brines whereas the other provides a horizontal solution to vertical tray columns used in refineries and other chemical plants. The third technology provides a more efficient, economical and operationally flexible form of distillation operation which can be used to separate suspended or dissolved solids and miscible liquids from water or other liquids. A US patent for the "Gas Hydrate Based Water Desalination" technology has recently been granted by the USPTO and an Indian patent is pending for this technology. A US, UK and Indian patent is pending for the "Horizontal Distillation Column" technology. A PCT application has been filed for "Simultaneous Evaporation and Condensation in Connected Vessels" technology. Complete work of Mr. Amit Katyal has been showcased on [www.eq-comp.com](http://www.eq-comp.com) website.

Mr. Amit Katyal is an independent researcher/ inventor based in New Delhi, INDIA. Mr. Amit Katyal is a Bachelor in Chemical Engineering from the Indian Institute of Technology, Delhi, INDIA and has a total experience of more than 20 years in hydrocarbon and water treatment sector in diverse segments like research, operations and technical services. Mr. Amit Katyal has developed some very useful softwares for hydrocarbon sector like EQ-COMP, HYD-PREDIC, LIQ-PROP, BUBBLE-SIM and MIX-CP. Additionally, Mr. Amit Katyal has also invented three patented/ patent pending technologies. One of the technologies gives usage of gas hydrate concept to desalinate high salinity brines whereas the other provides a horizontal solution to vertical tray columns used in refineries and other chemical plants. The third technology provides a more efficient, economical and operationally flexible form of distillation operation which can be used to separate suspended or dissolved solids and miscible liquids from water or other liquids. A US patent for the "Gas Hydrate Based Water Desalination" technology has recently been granted by the USPTO and an Indian patent is pending for this technology. A US, UK and Indian patent is pending for the "Horizontal Distillation Column" technology. A PCT application has been filed for "Simultaneous Evaporation and Condensation in Connected Vessels" technology. Complete work of Mr. Amit Katyal has been showcased on [www.eq-comp.com](http://www.eq-comp.com) website.



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