

# Crude oil assay and tbp distillation curves



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Crude oil is a complex mixture of hydrocarbon that formed naturally underground from remains of plant and animal that died and sank to the ocean floor with sand covered over millions of year. Under the high pressure and heat from the earth turned them into crude oil and natural gas where buried beneath the sedimentary rock. Crude oil is the unrefined raw material that will be extracted, processed and purified by refineries. Products from crude oil that produced fractionation are liquefied petroleum gas (LPG), kerosene, naphtha and diesel fuel etc.

### Crude oil composition

The chemical element composition of crude oil varies in widely from oilfield to oilfield, but the proportions of the element vary narrow limits. The composition of crude oil falls within the following range.

The main elements in crude oil are carbon and hydrogen which bonded and formed a compound called hydrocarbon. Hydrocarbon can be classified into four main chemical classes. The four main classes are the saturates, aromatics, resins and the asphaltenes.([3] NASKE. PDF) As the elemental analysis is unattractive because it gives limited information about the constitution of petroleum, hydrocarbon group type analysis is employed instead. Crude oil has impurities such as traces of metals and oxygen. The presence of these substances may significantly affect refinery processes. Therefore, crude oil that will be refined should be appropriate with the available processes.

## **Crude oil assay and TBP distillation curves**

The refining companies evaluate their crude oil to determine the most desirable processing sequence to obtain the required products, their laboratories will provide data concerning the distillation and processing of the oil and its fractions.

### Crude oil assay

The chemical evaluation of crude oil is called crude oil assay. This has more detailed than a crude TBP curve. A complete crude assay contains some of the following data: [4] Refining process handbook

- Whole crude salt, gravity, viscosity, sulfur, light-end carbons, and the pour point.
- A TBP curve and a mid-volume plot of gravity, viscosity, sulfur, and the like.
- Light-end carbons analysis up to C8 or C9.
- Properties of fractions (naphthas, kerosenes, diesels, heavy diesels, vacuum gas oils, and resids). The properties required include yield as volume percent, gravity, sulfur, viscosity, octane number, diesel index, flash point, fire point, freeze point, smoke point, and pour point.
- Properties of the lube distillates if the crude is suitable for manufacture of lubes.
- Detailed studies of fractions for various properties and suitability for various end uses.

The results from crude oil assay testing provide detailed hydrocarbon analysis data for refiners, oil traders and producers. Assay data helps

refineries to determine the compatibility of crude oil with them. It also provides data to determine yield, quality, production, environmental and other problems from crude. Furthermore information obtained from the petroleum assay is used for client marketing purposes. Feedstock assay data are an important tool in the refining process.

### **TBP distillation curves**

The widely used evaluation method to investigate the yield of products that will be obtained from refineries is true boiling point (TBP) curves. TBP curves analysis conducts in a batch distillation with a large number of stages and high reflux ratio. TBP curves are plotted between temperature of the hydrocarbon material present and volume percent of distilled. TBP distillation curves are generally run only on the crude and not on petroleum products. Typical TBP curves of various crude oils are shown in Figures 2.

## **Crude Distillation Unit**

Crude oil distillation is a physical separation process that operates continuously. It separates crude oil, which is multi-components substances, by the great range of boiling points in. Crude oil distillation contains of a multiple of hydrocarbon, organic metals, in addition to sediments, water and waxes. Products from crude oil are separated into fractions by distillation according to their boiling points so that each of the processing units following will have feedstocks that meet their particular specifications. For achieving higher efficiency and lower cost the crude oil separation is divided into two steps. The first step is fractionating crude oil at the atmospheric pressure. And then feed the high-boiling bottoms fraction (topped or

atmospheric reduced crude) from the atmospheric still to the second fractionators operated at a high vacuum.

Vacuum distillation is a method of distillation that the operating pressure is lower than vapor pressure of mixture. It increases relative volatility of the component and reduces the temperature requirement at low pressure. The employment of vacuum distillation reduces the temperature that necessary to vaporize the crude at atmospheric pressure for separating heavy portion of crude.

At atmospheric, the high temperature required for separating heavy portion of crude causes thermal cracking to occur, with the resulting loss to dry gas, discoloration of the product, and equipment fouling due to coke formation. Typical fraction cut points and boiling ranges for atmospheric and vacuum still fractions are given in tables 2 and 3.

The energy efficiency of crude oil fractionating process is also improved by adding complexity due to side-stripper and pump-around. Pump-around is used to condense vapor inside column and can increase energy efficiency by exchanging heat with other process stream usually feed stream to recovered heat by preheating its. Side strippers also increase heat recovery same as pump-around, it exchanges heat to feed stream before stores in storage tank or feeds to the next process.

## **Heat Integration of Distillation**

Heat integration is the way to improve process to the best energy efficiency by using heat exchanger network (HEN) synthesis. The current standard heat integrations are two main synthesis methods for researching HEN retrofit.

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The first is the pinch technology that based on thermodynamics. Another method is optimization method by using mathematical programming. (Tjoe and Linnhoff et al., 1986)

Pinch technology optimizes a HEN based on thermodynamics properties of process streams that energy saving and cost targets are important to design the HEN. The objective of pinch analysis is to maximize the process-to-process heat recovery and minimize the utility requirements of a system (T. Hallberg et al.,). The idea of the pinch point was introduced by (Umeda et al.,) and mainly developed by Linnhoff and Hindmarsh in the early of 70's. The pinch point (Shokoya 1992), where the minimum temperature difference,  $\Delta T_m$ , between two streams is observed determines the degree of possible heat recovery. The minimum temperature difference is called Heat Recovery Approach Temperature (HRAT). The process is divided by pinch point into two parts: above the pinch and below it. Each part of the process is in enthalpy balance. According to thermodynamics, there is no heat transfer across the pinch. But if there is heat transfer across the pinch, it was called criss-cross. The criss-cross matching was believed to give a lower cost solution comparing to the vertical matching. Pinch technology results a reduction of the overall energy requirements of the system. Furthermore the user can optimize the exchanger location as well as exchanger area. The maximum process-to-process heat exchange is at a certain  $\Delta T_m$ . The utility requirement decreases with the increase of heat recovery and the additional amount of heat exchanger area, so  $\Delta T_m$  should satisfy the system. The disadvantages of this method are the result cannot describe precisely where the additional areas are added and how many

networks restructure modifications such as re-piping, re-routing are required.

Mathematical programming is another method that is a simultaneous technique. It has been attended by researcher over two decades. A mixed Integer Linear Programming (MILP) proposed by Barboro and Nguyen. It is able to perform real-world optimizing scenarios for example non-isothermal mixing, exchanger relocation and re-piping costs. The exchanger area can be manipulate variously such as added as a new shell, area reduced by plugging tubes, and area reduced by passing exchanger, these manipulation affects the cost of exchanger. MILP can manipulate the objective function to optimize cost and profit variables and to generate the optimal flowsheet with various design constraints. Yee and Grossmann (1987) developed the MILP assignment-transshipment model to predict the retrofit model at a certain HRAT. The model distributes heat between hot and cold streams quickly and effectively but at a fixed level of energy recovery and did not take into account the exchanger cost obviously. Furthermore, they developed a two-step approach. First, they attempt to estimate cost for additional area requirements by transshipment model to do retrofit at difference energy recovery levels although it gives the overestimate this requirements. Then optimal solution determined in MILP is used to optimize using MINLP. Although the network structure is simplified, solving the MINLP model was still time consuming task and solution are still very often trapped at local optimum. Ciric and Floudas (1990) solved the pseudo-pinch problem by combining two-steps into a single step by using a MINLP to optimize heat exchanger area, energy reassignment and other features of a HEN. They

used HRAT to utility levels and used temperature interval approach temperature (TIAT) in partitioning the temperature range to controls the amount heat flow across pinch. Asante and Zhu (1997) developed retrofit HEN design that combined that features of mathematical optimization techniques based on thermodynamic analysis and practical engineering. They defined the approach temperature difference at which this occurs as the network pinch that indentifies the bottleneck of the network and the most effective change. They developed two-stage retrofit methodology. The first stage is MILP model which the existing topology is modified with a minimum number of promising HEN topology changed to achieve a desired heat recovery target. The topology changes suitable for retrofit design are a relocation of an existing heat exchanger associated piping in a different position within network and addition of a new exchanger match or a new split. The modified topologies will be then optimized using non-linear programming optimization technique (NLP) to find the most economic-attractive topology. This methodology indentifies a single topology change at a time and yields a sub-optimal solution. The sensible user interaction is required for achieving a meaningful result.

Recently, the results including the work of heat integration and heat exchanger network syntheses have been the topic of an important research activity in systematic process engineering.

Shenoy (1995) improved heat recovery of existing chemical processes through various retrofit techniques: computer search, mathematical programming, inspection and pinch technology. Jones et al., (1986) has suggested a step-wise approach that mostly relies on the use of simulation.

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A computer search technique is used to choose number of simulated maximum energy recovery (MER) networks and select the most economic-attractive and minimal change. The proposed network modification will be close to achieving the minimum utility target. The limitation of this method is the largely trial and error which does not clearly address how to systematically determine the required structural and parametric modifications in the network. However, Tjoe and Linnhoff (1987) discussed about the retrofitting method by inspection and computer search cannot guarantee to an optimal solution, while the application of mathematical programming is a powerful technique for retrofitting HENs. The retrofit of HEN by pinch technology has successfully used in a wide range of industries.

To achieving energy saving in a plant, the first solving technique for a retrofit example problem is an inspection, which is a tried technique therefore pinch technology is applied to solve problem more systematically. Then a retrofit-fixed heat transfer coefficient provides network modifications to achieve set targets. Targets can be set as energy and/or area savings as the concept of area efficiency. Tjoe and Linnhoff (1986) plotted investment vs. savings is used to obtain a target for retrofit design.

Although many HEN optimization issue have been proposed, those techniques have limitations, which cannot applicable with industrial efficiently. Mathematical programming has been developed to account for minimizing total cost in HEN design and retrofit problems (Floudas; 1995, Biegler et al., 1996). Turkay and Grossman (1996) applied disjunctive programming techniques to optimize systems with discontinuous investment costs. Nelsen et al., (1997) have shown features of practical importance

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applied with industrial HENs that cannot be considered in current HEN design methods. Later that feature presented in the literature, it overcame the traditional limitations of mathematical programming based method for optimizing HEN. It also provided the study systematically synthesis, design and operation issues in crude preheat system. Previously, Papalexandri and Pistikopoulos (1993) applied mass/heat exchange-based process representation framework to model enhanced heat integration possibilities. The model allows different streams, of temperature dependent heat capacities, can be mixed and lose their identity and intermediate streams processing can be obviously account for. Kralj and Glavić (1997) developed a method of sequential optimization of retrofits using the combination of pinch analysis, improved optimization procedure and MINLP and NLP algorithms.

Athier et al., (1998) used simulated annealing (SA), which is a NLP algorithm, procedure to propose modification of HENs. The procedure derived from a grassroot design model and used to optimize the structure. Papalexandri and Patsiatzis (1998) increased heat integration flexibility by allowing different stream mixing and intermediate stream processing. The procedure has systematically manner such as realistic heat exchange models considered to calculate actual area requirements, multiple objectives and trade-offs investigated systematically. The modified network showed the significant savings of a simultaneous optimization framework that is realizable for industrial systems, without prohibitive computational requirements.

Briones and Kokossis (1999) combined the use of thermodynamics and mathematical programming techniques into two-step approach. The first

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step is screening step, two MILP models (HEAT and TAME model) are used for auditing existing network as well as screening of the most promising topology and addition heat exchanger area. Range area targets were calculated and show the result into an investmenti€saving plot. These MILPs are employed by targeting procedure and determine the trade off among energy, number of units, structural modification all possible configurations within network.

Markowski (2000) applied pinch technology-based approach which is founded in many industrial applications to retrofit HEN. This advantage of this technique is user-friendly and its application can use with various design problems.

Bulasara and Uppaluri (2009) studied revamping of the crude distillation unit (CDU) HEN based on pinch design method with and without the free hot streams available in the delayed coking unit (DCU). In this study contained two sub-cases: first is installation of new exchangers for the entire method and second is reutilization of existing heat exchangers. The results from this research showed that the most promising option is the partial modified CDU HEN with free hot streams with free hot streams available from DCU.

Smith et al., (2010) studied the methodology for retrofitting of HENs based on pinch analysis. They developed the methodology from Asante and Zhu (1997) which contains two steps: structure modification and cost optimization steps – into a single step. It also improves the thermal properties of stream to depend on temperature which approaching to the

real situation. This design method avoids missing cost-effective design solutions.

From the above researches, the retrofit of heat exchanger networks for crude distillation unit with mathematical programming is the most effective technique that gives the optimal solutions as the set objective function. This technique also saves time significantly.