Thermophysical properties control during transportation of the liquefied hydrocarbon mixtures by means of REFPROP software package

G S Zakirova¹, E I Krapivsky²

¹ Saint-Petersburg Mining University, 2, 21 Line, Saint-Petersburg, 199106, Russian Federation
² Ukhta State Technical University, 13, Pervomayskaya St., Ukhta, Republic of Komi, 169300, Russian Federation

E-mail: gulnur-live@mail.ru

Abstract. The authors have presented an argument for the possibility of REFPROP software package application for thermophysical properties control of the liquefied hydrocarbon mixtures depending on the composition including design and measured data of phase states of the hydrocarbon mixtures. The studies were carried out by the example of the Chayandinskiy oil and gas condensate field. The presented results of the phase state of mixtures of an oil and gas condensate field using the example of the Chayandinskiy field allow us to predict the behavior of liquefied hydrocarbons at low temperatures, as well as determine the parameters for further transportation in a single-phase liquid state through low-temperature pipelines. Also the task of thermophysical properties control during transportation of the liquefied hydrocarbon mixtures has been analysed. The composition changing of methane and light hydrocarbon mixture allows one to enlarge the mixture density greatly and to change its other properties at acceptable temperatures and pressures. In the article it is shown that the mixture usage is energetically more efficient than the liquefied gas.

1. Introduction

The authors are working out the technology of transportation of natural gas, gas condensate and oil fractions in the liquefied state from oil, gas and condensate fields through main pipelines [1, 2]. Herewith the volume of the liquefied gas decreases 300 – 400 times, the diameter of the pipeline decreases several times, as a consequence the pipeline price also decreases several times [3, 4]. So it is not necessary to build the pipelines for oil and condensate (a condensate pipe). And the construction period is shortened. In order to be able to transport the gas mixture through the main pipelines at allowable temperature (minus 50 °C) and pressure (up to 12 MPa), unstable gas condensate and oil from the producing fields are added to natural gas (wet methane) in the ratio of (3 - 10 %) which is designated by the experimental or software method.

The aim of the present research is to study the possibility of thermophysical properties control during the transportation of the liquified hydrocarbon mixtures. The liquified hydrocarbon mixture is meant to transport through the low-temperature main pipelines in the single-phase liquid state. The design temperature of liquafaction is minus 40 °C (with the set temperature of minus 50 °C), and the design pressure is 12 MPa (taking into account liquafaction up to 10 MPa).
2. REFPROP software package application for calculation of the phase equilibrium (PE) and the thermophysical properties (TP) of the multicomponent hydrocarbon systems at different temperatures and pressures

In the authors’ research works the PE and TP REFPROP licenced specialised thermodynamic library is used for calculation of the diagrams P–T–ρ (pressure – temperature – density), P–T–H (pressure – temperature – entropy) and others. The REFPROP library (the full name is «Reference data base NIST 23») is worked out by the National Institute of Standards and Technologies of the USA and is considered actually as a world-wide standard used for the high precise calculation of the physical properties of straight products and mixtures for cooling fluids, hydrocarbons and components of natural gas [5 - 8]. Thermodynamic properties and their derivatives are calculated including transportation properties (viscosity, heat conductivity, surface tension and dielectric constant, higher and lower heating value) (Figure 1) [5].

![Figure 1. The dialogue box of substance properties choice in the medium of REFPROP software application.](image)

The system calculates the mixtures properties with the involvement of the collaborative function that is determined according to the experimental data concerning thermodynamic properties (TDP) for the examined mixtures and according to the extended equation for non-examined mixtures. The version of 9.1 system provides the calculation of 49 thermophysical properties of 100 pure substances and 145 mixtures. Also users will be able to determine TDP of the mixtures with the composition which is set up by them if the calculation model applied in the system can be used for mixture components.

According to the results, the software application allows one to build up and look through the calculation results in the form of tables with different values of the reference parameters, to construct diagrams of TP change and phase diagrams in different coordinates. They are temperature – entropy, temperature – enthalpy, temperature – density, pressure – enthalpy, pressure – density, pressure – volume, pressure – temperature, compression coefficient – pressure, viscosity – temperature, temperature – composition (only for binary mixtures), pressure – composition (only for binary mixtures), etc.

3. Examination of the phase states of the liquefied hydrocarbon mixtures at the Chayandinskiy gas-condensate field with the use of REFPROP software application

It is necessary to choose transportation parameters correctly – pressure P and temperature T – to provide the single-phase liquid state of the liquefied hydrocarbon mixtures along the whole length of the pipeline [9]. For these reasons it is necessary to study the phase state of the hydrocarbon system by means of determination of the critical values (critical pressure and critical temperature) [10].
The major field for building the Yakutskiy center of gas extraction is the Chayandinskiy oil, gas and condensate field. For product transportation and gas condensate and oil involvement into refining we suggest to build an underground low-temperature pipeline from the Chayandinskiy field up to the «Eastern Siberia – The Pacific Ocean» pipeline with a 720 mm diameter and the length of about 130 – 200 km on the installation for complex processing of gas, condensate and oil (UKPGKN) in Lensk. It is suggested to divide the mixture into methane component, gas condensate and oil component on the UKPGKN in Lensk. After regasification it is worth pumping methane and ethane into the pipeline «Power of Siberia»; unstable gas condensate and oil fraction should be delivered to the gas-and-oil refining plants or should be pumped into the oil pipeline «Eastern Siberia – The Pacific Ocean».

It will make possible to:
- refuse from condensate pipeline and oil pipeline building;
- provide oil to oil-refineries and condensate to gas refining plants.

The research work was carried out in terms of the Chayandinskiy oil, gas and condensate field (Table 1). The analysis of phase states of the liquefied carbohydrates mixtures at low temperatures was carried out for providing pumping-over of the liquefied carbohydrates mixtures through low-temperature pipelines in the single-phase liquid state [11].

**Table 1.** The conventional compositional analysis of gas, gas condensate and light oil of the Chayandinskiy oil, gas and condensate field and typical natural gas.

| Components | Chemical formula | Gas, mass percent | Gas condensate + light oil, mass percent of gas | Typical natural gas, mass percent of gas |
|------------|------------------|-------------------|-----------------------------------------------|------------------------------------------|
| 1 methane  | CH₄              | 69.26             | 3.84                                          | 88.8                                     |
| 2 ethane   | C₂H₆             | 8.26              | 3.43                                          | 3.21                                     |
| 3 propane  | C₃H₈             | 4.61              | 6.5                                           | 0.61                                     |
| 4 iso-butane+ | iso-C₃H₁₀+      | 6.44              | 24.3                                          | 0.295                                    |
| n-butane+  | iso-C₃H₁₀+       |                   |                                               |                                          |
| 5 propane  | C₄H₁₀            | 6.38              | 61.3                                          | 0.4                                      |
| 6 hydrogen sulphide | H₂S | 0         | 0                                             | -                                        |
| 7 carbon dioxide | CO₂ | 2.25     | 0.509                                         | 6.54                                     |
| 8 nitrogen | N₂              | 2.5               | 0.12                                          | 0.145                                    |
| 9 helium   | He               | 0                 | 0                                             | -                                        |
| 10 hydrogen | H₂              | 0.03              | 0                                             | -                                        |
| 11 sum     |                  | 100.0             | 100.0                                         | 100.0                                    |

The diagrams of gas and oil phase states of the Chayandinskiy field are schematically indicated in Figure 2. In Table 2 there are critical values of the liquefied carbohydrates mixtures with the different content of gas condensate and light oil of the Chayandinskiy field which are calculated by means of REFPROP ver. 9.1 software application.

**Table 2.** Critical values of the gas and gas condensate mixtures of the Chayandinskiy oil, gas and condensate field at a different ratio of pure methane and typical natural gas.

| Component s | Design ation | Methane | Typical natural gas | Mixture of gas and gas condensate, mass percent of gas |
|-------------|--------------|---------|---------------------|-------------------------------------------------------|
| 1 Critical temperature °C | -82.59 | -73.15 | -50.64 | -39.58 | -37.1 | -35.01 | -28.79 |
| 2 Critical pressure MPa | 4.59 | 5.36 | 8.71 | 9.99 | 10.45 | 10.83 | 11.72 |
Figure 2. Schematic representation of the diagrams of gas and oil phase states of the Chayandinskiy field.

Reference designations: \( P_c \), \( t_c \) – critical pressure and temperature respectively; indexes: Ch – Chayandinskiy.

The P-T (pressure – temperature) phase diagram of the mixture at a ratio of 97% of nature gas and 3% of gas condensate (Figure 3) which is plotted by means of REFPROP ver. 9.1 software application. In Tables 3 - 5 changing of the phase states of carbohydrates mixture at different temperatures \( T_1 = -55 \, ^\circ C \), \( T_2 = 0 \, ^\circ C \) and \( T_3 = 55 \, ^\circ C \) is indicated during pressure changing.

Figure 3. The pressure-temperature diagram (P – T) of gas, gas condensate and light oil mixture at the ratio of 97% and 3% mass percent.

Table 3. Table of phase states change of the carbohydrates model mixture at \( T_1 = -55 \, ^\circ C \) during pressure change.

| Temperature (°C) | Pressure (MPa) | Density (kg/m³) | Enthalpy (kJ/kg) | Entropy (kJ/kg·K) | Phase     |
|-----------------|---------------|-----------------|-----------------|------------------|-----------|
| 1               | - 55.0        | 1.0             | 13.22           | 516.89           | 3.51      | 2-Phase   |
| 2               | - 55.0        | 7.0             | 238.71          | 316.01           | 2.04      | 2-Phase   |
| 3               | - 55.0        | 7.49            | 320.44          | 283.09           | 1.88      | Liquid    |
| 4               | - 55.0        | 15.0            | 357.74          | 272.32           | 1.73      | Liquid    |
| 5               | - 55.0        | 19.0            | 369.73          | 272.08           | 1.68      | Liquid    |
Table 4. Table of phase states changing of the model mixture of carbohydrates at $T_2 = 0 \, ^\circ C$ during pressure changing.

| Temperature ($^\circ C$) | Pressure (MPa) | Density (kg/m$^3$) | Enthalpy (kJ/kg) | Entropy (kJ/kg·K) | Phase          |
|--------------------------|----------------|--------------------|------------------|-------------------|----------------|
| 1                        | 0.0            | 1.0                | 9.68             | 687.60            | 2-Phase        |
| 2                        | 0.0            | 13.0               | 203.58           | 502.40            | 2-Phase        |
| 3                        | 0.0            | 14.03              | 225.21           | 491.13            | Supercritical  |
| 4                        | 0.0            | 15.0               | 236.77           | 483.58            | Supercritical  |
| 5                        | 0.0            | 19.0               | 271.45           | 464.13            | Supercritical  |

Table 5. Table of phase states changing of the model mixture of carbohydrates at $T_3 = 55 \, ^\circ C$ during pressure changing.

| Temperature ($^\circ C$) | Pressure (MPa) | Density (kg/m$^3$) | Enthalpy (kJ/kg) | Entropy (kJ/kg·K) | Phase          |
|--------------------------|----------------|--------------------|------------------|-------------------|----------------|
| 1                        | 55.0           | 1.0                | 7.74             | 838.57            | Gas            |
| 2                        | 55.0           | 4.18               | 34.73            | 804.40            | Gas            |
| 3                        | 55.0           | 5.0                | 42.36            | 792.81            | 2-Phase        |
| 4                        | 55.0           | 9.0                | 82.73            | 748.54            | 2-Phase        |
| 5                        | 55.0           | 10.21              | 95.88            | 737.26            | Supercritical  |
| 6                        | 55.0           | 15.0               | 147.58           | 691.01            | Supercritical  |
| 7                        | 55.0           | 19.0               | 185.17           | 663.12            | Supercritical  |

Consequently, in accordance with the set task the mixture of liquefied carbohydrates at temperatures of minus 50 to minus 40 °C and high pressure (10 – 12 MPa) will be in the liquid phase. The given results of the mixtures phase state of the oil, gas and condensate field using the example of the Chayandinskiy field allow one to predict the reaction of liquefied hydrocarbons at low temperatures as well as to determine the values for its farther transportation in the single-phase liquid state through the low-temperature pipelines.

4. Thermophysical properties control during transportation of the liquefied hydrocarbon mixtures

Given in Figures 4, 5 and 6 (7, 8 and 9) the «pressure – temperature – density» («pressure – temperature – enthalpy») relationships of the mixture show the possibility of great changing of thermophysical properties of the liquefied hydrocarbons.

Figure 4. $P – T – \rho$ (pressure – temperature - density) diagram for pure methane.
Addition of 20% propane in mass increases the mixture density in comparison with pure methane at a temperature of 20 ºC up to 250 kg/m³ (by 20%) and at a temperature of -20 ºC up to 300 kg/m³ (Figures 4 and 5). At the same time the mixture enthalpy also greatly increases (heat content and thermal content). Addition of 20% C₆H₁₄ hexane increases the mixture density even more (up to 310 kg/m³ at a temperature of – 20 ºC) (Figure 6).
Figure 8. P – Т – Н (enthalpy) diagram for the mixture of 80% of methane (mass percent) and 20% of propane

Figure 9. P – Т – Н (enthalpy) diagram for the mixture of 80% of methane (mass percent) and 20% of hexane.

5. Conclusion
The following conclusions can be made:
  1. The composition changing of the methane and light hydrocarbons mixture allows one to increase the mixture density greatly and many other its properties at an acceptable temperature and pressure.
  2. Applying the mixture is energetically more economical than the liquefied gas.
  3. Applying the compressed mixture of methane and gas condensate for heat and gas supply allows one to exclude oil gas flaring, to reduce costs for gas condensate transportation, to increase heat value of the mixture.

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