Effect of pour point depressants and diluents on exergy destruction during pipeline transportation of crude oil

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Abstract. Exergy destruction in pipeline flow of crude oils mixed with pour point depressants (PPD) and diluents has been investigated. Ethylene vinyl acetate with vinyl acetate content of 18% and 28% (EVA-18 and EVA-28) and Polymethyl methacrylate (PMMA) with concentrations of 200 ppm, 1000 ppm and 1500 ppm were chosen as the PPDs for this purpose. Four different diluents were considered viz. n-hexane, cyclohexane, n-butanol and toluene representing paraffins, naphthenes, alcohols and aromatics respectively. The viscosity reduction was found out experimentally. Using these results for a hypothetical pipeline, the effect of API gravity of crude oil, pipeline diameter, Reynolds number, PPD concentration and diluent type on exergy destruction was investigated. These findings would help in making a prudent choice of PPD and diluents for efficient transportation of crude oil through pipelines.

1. Introduction

Pumping of viscous crude oil for long distance transportation results in major energy consumption [1]. It leads to high operating costs and hence overall economic loss. Pumping process is highly irreversible. Detailed second law analysis of this process is highly essential to identify the irreversibilities and reduce the same. These irreversibilities can be due to friction, heat transfer, concentration gradient, mixing or chemical composition. Such irreversibilities can be measured with the help of exergy. Exergy is the maximum amount of useful work that can be obtained in a given environment [2]. The more the irreversibility, greater is the reduction in the exergy and the more the exergy loss, higher is the consumption of energy that drives the process. Hence the exergy analysis of a process gives better insight into the energy consumption and subsequently the economic loss.

Exergy can be classified into physical and chemical exergy. The exergy due to heat, pressure and flow can be considered as physical exergy whereas the exergy of chemical reaction and mixing comes under chemical exergy. Physical exergy is a function of temperature, enthalpy, entropy and hydraulic resistance whereas the chemical exergy is mainly a function of the Net Heating Value (NHV) and the mole fraction of the components. In case of crude oil, these factors are more pronounced due to the changes in wax precipitation behaviour at different ambient conditions. Cheng [3] has studied the effect of wax deposition on physical and chemical exergy of a crude oil pipeline in China.
It has been found that the unavoidable exergy loss in transportation of crude oil is mainly dependent on various factors like the outbound temperature, outbound flow and outbound pressure. Pal [4] has studied the exergy destruction of a surfactant stabilized oil-in-water emulsion. Nyugen [5] has discussed component by component calculation method for more accurate prediction of physical exergies. Using the case study of Yamal-Europe gas pipeline, Chaczyszewski [6] has done the exergy analysis of the gas transmission system. Govin [7] has developed the correlations for estimating the chemical exergies of fuels and petroleum fractions. Rivero [8] has developed a method to calculate the exergy of crude oil mixtures. Calculation of exergies is a tedious procedure especially for hydrocarbons. This has been addressed by Abdollahi-Demneh [9] and Montelongo-Luna [10] by developing procedures in process simulators and online tools for calculating the physical and chemical exergies.

Pour point depressants and diluents are generally used to reduce the apparent viscosity of crude oil during transportation through pipelines with lesser pumping power. Proper combination of crude oil and the PPD or diluent helps to reduce the exergy destruction during pumping and improves the economics of the overall transportation process. Literature survey suggests that the exergy analysis of pipelines carrying crude oil mixed with pour point depressants and diluents has not been studied in details. Hence an attempt has been made to perform the exergy analysis of such systems. This work studies the effect of various parameters like the pipeline diameter, Reynolds number, API gravity of crude oil, concentration of the PPDs and type of diluents on the physical exergy for crude oils mixed with PPDs and diluents.

2. Materials and Methods

Crude oils (C1, C2 and C3) obtained from western parts of India were characterized for density at 15 °C, 0 API, wax content (%), asphaltene content (%), wax appearance temperature (WAT) (°C) and viscosity at WAT (N s/m2) as per the standard procedures. The properties are shown in Table 1.

| Table 1. Properties of crude oils used in the experimentation |
|-------------------------------------------------------------|
| C1  | C2  | C3  | Method          |
| Density (kg/m3) at 15°C | 875.4 | 877.0 | 887.0 | ASTM D1298 |
| 0 API | 30.1 | 29.8 | 28 | Formula |
| Asphaltene content (%) | 12.2 | 5 | 7.2 | IP 143, ASTM D 6560 |
| Wax content (%) | 25.1 | 35.5 | 45.7 | ASTM UOP 46-85 |
| Pour Point (°C) | 18 | 27 | 33 | ASTM D-97 |
| WAT (°C) | 30 | 43 | 50 | Viscometry |
| Viscosity at WAT (N s/m2) | 0.0693 | 0.0554 | 0.0821 | Brookfield DVII+ Pro Viscometer |

Two types of pour point depressants (PPD) viz. linear and comb shaped were chosen for study. Ethylene Vinyl Acetate (EVA) was chosen as the linear type having 18% and 28% of vinyl acetate content. The comb type PPD was Poly Methyl Methacrylate (PMMA). The PPDs were dissolved in appropriate solvents viz. xylene for EVA and ethyl acetate for PMMA in required proportions such that their final concentrations in the crude oil were 200 ppm, 1000 ppm and 1500 ppm.

The given samples of crude oils were treated with four different commercially available diluents viz. n-hexane, cyclohexane, n-butanol and toluene. The concentration of diluents chosen for experimentation was a constant value of 10%.

The viscosities of the above solutions (volume = 50 ml each) were measured. These viscosities were used for the further calculations of exergy.

A hypothetical crude oil pipeline 200 km long was considered to transport 10000 barrels per day of crude oil in an ambient temperature of 15°C. The above samples were considered to be transported through this pipeline. The diameters considered for the pipelines were 0.2032, 0.4064, 0.6096 and 0.7620 m (i.e 8, 16, 24 and 30 inches). The crude oil temperature was maintained at its WAT to avoid gelling and precipitation.
The flow exergy of a stream is a function of physical, chemical, kinetic and potential energy. The kinetic and potential components can be incorporated in the flow exergy calculations which includes pressure and temperature components. According to Chen [11], pressure exergy is a function of temperature and pressure only. They do not depend on the properties of crude oil. Since the flow in the above pipeline is considered at constant temperature maintained at WAT, thermal exergy is neglected. Hence the flow exergy considered here is the pressure exergy. This has been calculated using the following expressions derived by Pal [4] and the results have been discussed in the subsequent sections.

For laminar flow, the exergy destruction is given by

\[ E_{xD} = \frac{\pi}{2} \left( \frac{T_0}{T} \right) \left( \frac{\mu^3}{\rho^2 D^2} \right) (16 Re^2) \]  

And for turbulent flow, it is given by

\[ E_{xD} = \frac{\pi}{2} \left( \frac{T_0}{T} \right) \left( \frac{\mu^3}{\rho^2 D^2} \right) (0.079 Re^{2.75}) \]  

Where,

- \( E_{xD} \) = Exergy destructed (J),
- \( T_0 \) = Ambient temperature (K),
- \( T \) = Temperature of the crude oil (K),
- \( \mu \) = Viscosity (N s/m²),
- \( \rho \) = Density (kg/m³),
- \( Re \) = Reynolds number

3. Results and Discussion

Tables 2 and 3 show the viscosities of crude oils treated with the PPDs at different concentrations and diluents with concentration 10%. These results were used for calculating the exergy using equations (1) and (2).

| Crude Oil | PPD Concentration (ppm) | EVA-18 (N s/m²) | EVA-28 (N s/m²) | PMMA (N s/m²) |
|-----------|--------------------------|-----------------|-----------------|---------------|
| C₁        | 0                        | 0.0693          | 0.0693          | 0.0693        |
|           | 200                      | 0.0124          | 0.0143          | 0.0105        |
|           | 1000                     | 0.0119          | 0.0147          | 0.0095        |
|           | 1500                     | 0.0117          | 0.0192          | 0.0116        |
| C₂        | 0                        | 0.0554          | 0.0554          | 0.0554        |
|           | 200                      | 0.0182          | 0.0242          | 0.0105        |
|           | 1000                     | 0.0200          | 0.0356          | 0.0103        |
|           | 1500                     | 0.0224          | 0.0381          | 0.0102        |
| C₃        | 0                        | 0.0821          | 0.0821          | 0.0821        |
|           | 200                      | 0.0191          | 0.0225          | 0.0137        |
|           | 1000                     | 0.0194          | 0.0236          | 0.0138        |
|           | 1500                     | 0.0198          | 0.0251          | 0.0145        |

3.1. Effect of pipeline diameter and Reynolds number on exergy destruction

From Figures 1, 2 and 3 it is seen that the larger the pipeline diameter, the lesser is the exergy destruction and it decreases irrespective of the crude oil sample. Also, as the Reynolds number increases, the exergy destruction increases. The lesser diameter pipe has higher Reynolds number and hence the highest exergy destruction. This will result in greater pumping cost.
Table 3. Variation in viscosity due to diluents (10% concentration) for different crude oil samples

|           | C_1   | C_2   | C_3   |
|-----------|-------|-------|-------|
| Without diluent | 0.0693 | 0.0554 | 0.0821 |
| n-Hexane   | 0.0284 | 0.0163 | 0.0225 |
| Cyclohexane| 0.0321 | 0.0180 | 0.0229 |
| n-Butanol  | 0.0289 | 0.0224 | 0.0323 |
| Toluene    | 0.0252 | 0.0159 | 0.0207 |

Chen [11] had observed that pressure exergy destruction increases with increase in pressure. It was also observed that the greater the flow, more is the exergy loss. Chen [1] had varied the pipe diameter from 0.168 m to 0.323 m and found that the pressure exergy destructed decreased from 33 to 6 kJ/sec. In the present work, when the pipe diameter is varied from 0.2032 m to 0.7620 m, the exergy destructed decreases from 1.21 kJ to 0.006 kJ. As the flow rate of crude oil is increased, the exergy destructed first decreases and then increases. Thus, the present work yields the similar results as reported by Chen [1], [11]. The greater the irreversibility, higher is the exergy loss.

Figure 1. Exergy and Reynolds number vs Pipe diameter for C_1

Figure 2. Exergy and Reynolds number vs Pipe diameter for C_2
Figure 3. Exergy and Reynolds number vs Pipe diameter for C₃.

3.2 Effect of API gravity on exergy destruction at different pipeline diameters
Figure 4 shows the variation in the exergy destruction with the API gravity. The exergy destruction increases with decrease in the API gravity. Heavier oil will be more viscous and will generate more pressure drop. This leads to more exergy destruction. Also, as the diameter decreases pressure drop increases further and hence the exergy loss. Thus, a larger diameter pipeline is economical for heavier crude and vice versa. Hence the type of oil is a major factor in determination of exergy destruction.

3.3 Effect of PPD concentration on exergy destruction
Figures 5, 6 and 7 show the variation in exergy destruction with changes in PPD concentration for the crude oils C₁, C₂ and C₃. For a given crude oil the exergy destruction decreases with increase in the PPD concentration. But it does not have a linear trend. The exergy destructed decreases with increasing PPD concentration to an optimum value and then starts increasing. The minimum exergy destruction is found to be at around 400 ppm concentration of the PPD. Also, this minimum is more pronounced for PMMA as compared to EVA-18 or EVA-28. The reason for this is as follows. As seen from equations (1) and (2), the exergy destruction is directly proportional to viscosity. It has been seen that reduction in viscosity is more for comb-shaped PPDs like PMMA as compared to linear PPDs like EVA [12-13]. The structure of copolymers, especially the proportion of polar and nonpolar segments, plays an essential role in affecting the rheological properties of crude oil [14]. It has also been found that lower concentrations of PPDs are more effective in reducing the viscosity. Hence, the lower the concentration, better is the viscosity reduction. This is due to the fact that the PPDs associate themselves with wax crystals. An increase in the concentration of PPDs results in a larger network with wax thereby reducing the flow ability [15]. Further the wax to asphaltene ratios for C₁, C₂ and C₃ are 2.05, 7.1 and 6.34 respectively. It is observed that the more is the wax to asphaltene ratio, the more is the exergy destruction. This is in line with the observations of Chen [10] who had observed that waxy crude oil contributed to more exergy loss. This has been attributed to the changes in chemical exergy which results from the wax precipitation. Wax precipitation leads to changes in density, viscosity and heat capacity which in turn changes the chemical exergy.
Figure 4. Exergy Destruction vs API gravity for various pipe diameters

Figure 5. Exergy Destruction vs PPD concentration (EVA-18) for different crude oils

Figure 6. Exergy Destruction vs PPD concentration (EVA-28) for different crude oils
3.4 Effect of type of diluent on exergy destruction

Figure 8 shows the exergy destruction for crude oils C₁, C₂ and C₃ mixed with different diluents. It was found that the exergy destruction for toluene was the least. The trend followed with respect to exergy destruction in increasing order was

Toluene < n-hexane < Cyclohexane < n-butanol.

The reduction in viscosity has been observed in the following order.

Toluene > n-hexane > Cyclohexane > n-butanol.

The variation of viscosity due to addition of diluents to oil depends on the chemical interactions between the diluents and the oil constituents. These interactions depend on the Hansen Solubility Parameter of the diluents [16]. Hansen has suggested that the solubility parameter comprises of three types of interactions viz. (a) Dispersion (London) forces which correspond to the van der Waals interactions ($\delta_D$) (b) Polar interactions due to charged species ($\delta_P$) (c) Hydrogen bonding ($\delta_H$). The Hansen parameters for the diluents used in the experimentation have been given in Table 4. Toluene has the highest Hansen solubility parameter for dispersion as compared to the other diluents. Moreover, it’s polar as well as the hydrogen bonding parameter have moderate values. In case of n-hexane, the Hansen parameters representing polar and hydrogen bonding are zero. This prevents its interaction with the polar components of crude oil. Also, no hydrogen bonding is possible. Hence the viscosity reduction takes
place by simple dilution effect. The presence of Hansen hydrogen bonding parameter in cyclohexane contributes to the increase in the hydrogen bonding. This results in lesser viscosity reduction than \( n \)-hexane. Also, the absence of polar part of the Hansen parameter in it, reduces the viscosity reduction as compared to toluene. \( n \)-butanol gives the least viscosity reduction. Gateau [17] has found that the large hydrogen bonding parameter of alcohols is responsible for their inability to sufficiently reduce the viscosity of crude oil. Hence, amongst all the diluents, toluene contributes to highest viscosity reduction and subsequently less exergy destruction.

| Diluent     | \( \delta_p (\text{MPa}^{1/2}) \) | \( \delta_T (\text{MPa}^{1/2}) \) | \( \delta_H (\text{MPa}^{1/2}) \) |
|-------------|---------------------------------|---------------------------------|---------------------------------|
| \( n \)-hexane | 14.9                           | 0.0                             | 0.0                             |
| Cyclohexane  | 16.8                           | 0.0                             | 0.2                             |
| \( n \)-butanol | 16.0                          | 5.7                             | 15.8                            |
| Toluene      | 18.0                           | 1.4                             | 2.0                             |

4. Conclusion
The exergy destruction of crude oil transportation when mixed with pour point depressants and diluents has been studied. It is found that the exergy destruction decreases as the crude oil viscosity decreases. The chemical composition of crude oils especially the wax content and the asphaltene content as well as the type of PPDs and the diluents affect the overall exergy destruction. A wise choice of the PPDs and diluents will give better viscosity reduction and will help in reducing the pumping power and the economics of the transportation process. The present study has not taken into account the chemical exergies of the crude oil, PPDs and diluents. More detailed study involving the mixing effect of these along with the physical exergy needs to be undertaken to get a better insight into the overall exergy destruction.

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