

Feasibility study about adding DSO to Hydrocarbon Condensate

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This work presents a feasibility study about the injection of the DSO-a side product in LPG treatment units - to Hydrocarbon condensate- product of stabilizing units- in South Pars Gas Complex phases 4, 5 plants. 5.2 ton/day DSO (Disulfide Oil) is produced in LPG a unit which uses caustic for removing mercaptane from LPG and as a waste side product; it is burned in burn pit. The Hydrocarbon condensate is separated from the plant feed by the rate of 80000 bbls /day and stored as a product after RVP adjustment. A PVTsim and HYSYS simulation followed by a sort of lab experiments and the following results are achieved. The total sulfur and mercaptane content of Hydrocarbon condensate are 2830 ppmw and 2300 ppmw respectively which this injection increase the total sulfur up to 3380 ppmw. This amount meets the Hydrocarbon client's standards. The lab experiments are shown a decrement in Hydrocarbon condensate density. Concluding from simulations' results the DSO, Hydrocarbon mixture in operating pressures (1 to 50 barg) formed wax at -41 to -37 degree centigrade so in the positive operating temperature of the plant, there is no risk of wax formation. Low amount of caustic which exist in DSO, should be separated before injection. Injecting DSO to hydrocarbon condensate increases the DSO selling price and in the other hand decreases the environmental pollution of DSO burning.

Keywords: DSO, Condensate, injecting DSO

Introduction

The SOUTH PARS gas field is in Iran and is the North Eastern side of a large structure located in the Persian Gulf, known in Qatar as the North Field. The field is located offshore around 100 km south of Asaluyeh. The onshore receiving facilities and gas treatment plant are located on the Iranian coast of the Persian Gulf near Asaluyeh village.

Hydrocarbons are found in several intervals, which the most important reservoir is the Khuff carbonated, around 3000 meters below ground, with a thickness of approximately 450 meters. The field is the largest gas field in the world.

28 phases was predicted for development of this gas field in Iran side. Each gas phases was designed for processing of 1000 MMSCFD of raw gas plus with 40000 bbl/day condensate, including offshore production platforms, under sea pipe lines and onshore processing facilities. The reservoir fluid mixed with MEG in order to avoid risk of hydrate formation in the presence of free and saturated water.

Condensate stabilizing process

In the Phases 4&5 gas plant, two 32" sea lines originating from the wellhead platforms, route multi-phase flow (gas, condensate and glycolated water) to reception facilities in onshore. Raw feed received from two platforms, normally bypasses the pig receivers and flows via a manifold to a finger-type slug catcher. Subsequent to reception of the sea line fluids, the gas is separated from the liquids in the slug catcher and then in the HP Separators. Separated raw gas and liquids routed to gas treating and condensate stabilization units respectively. The function of condensate stabilization unit is to remove the lightest components (off-gas) from the raw feed and to produce a liquid product, which after mixing with the (C₅⁺) from NGL fractionation unit, will give 80,000 bbl/day stabilized condensate having a Reid Vapor Pressure (RVP) of 10 psia in summer and 12 psia in winter.

LPG treating process

Propane and butane cut produced by the upstream NGL Fractionation are treated in LPG treating units. The purpose of the units is to remove Sulphur compounds and mercaptans from LPG, prior to dry them so as to comply with commercial grade specifications. The design is based on the use of a caustic soda wash process with caustic soda regeneration by direct oxidation with air in the presence of a proprietary catalyst. About 5.2 ton/day Disulphide Oil (DSO) is produced in these units as a by-product. DSO should be stored for further export to other external users.



Problem Description

As it mentioned before, produced DSO should be stored in relevant storage tank and due to caustic carry over, draining needs to be done occasionally and caustic sent to neutralization package.

When there is no market for DSO, production should be sent to burn pit while storage tank is full. Burning DSO causes sulfur compounds conversion to sulfur oxides and consequently air pollution. An alternative method is mixing DSO with stabilized condensate.

Table1. Physical Properties of Stabilized Condensate

Stabilized Condensate	
Composition	RVP: 10 psia in summer/12 psia in Winter Water: < 500 ppmv RSH: <2400ppmw H ₂ S: <20ppmw
Conditions	Temperature : 37.1°C summer; 28.6°C winter Pressure : 10.4 barg Density : 736 kg/m ³

Table2. Physical Properties of DSO

DSO	
Composition	DMDS :20-22 mol% DEDS : 77-79 mol% Water : few hundred of wt ppm NaOH : traces LCPS30 Catalyst : traces
Conditions	Temperature: 45 to 50°C Pressure : 5 barg Density : 979-1030 kg/m ³ Viscosity: 0.85 cp

The pros and Cons of Mixing DSO and Stabilized Condensate

Mixing DSO and stabilized condensate have got different advantages and disadvantages as following:

Advantage of mixing

1. Solving DSO storage problem
2. Preventing DSO burning and so air pollution
3. Exporting DSO with condensate which means value added

Disadvantage of mixing

There are different disadvantages from process and operational points of view:

✓ Operational Problems:

1. There is no line between LPG treating and condensate storage tanks, but a pump connected to DSO storage tank can be linked to condensate storage unit. Now, DSO is routed to burn pit via a connection located at the bottom of its storage tank. As carried over caustic accumulated at the bottom of tank, using bottom connection can leads to caustic transfer to condensate storage tanks. So a new connection point should be considered for sending DSO to condensate storage unit. In addition, safety and controlling points need special attention.

✓ Process Problems:

1. Produced DSO is polluted with caustic, sulfide and sulfite salts and MEROX catalyst, which salts can plug lines and caustic can cause corrosion in valves, lines and condensate storage tanks.
2. Usually mercaptan content and total sulfur of stabilized condensate are 2300 ppmw and 2830 respectively. Whether 5.2 ton/day DSO is injected to 80,000 bbls of condensate, total sulfur will increase about 550 ppmw (1300 ppmw). According to design documents, there is no specification for total sulfur, but it seems acceptable limit for international shipping is 3000 ppmw.

Investigation about Wax Formation for mixture of DSO and Condensate Using Software

PVTSim used to check possibility of wax formation in mixture of DSO and condensate. For simulation, required streams and their physical and chemical characterizations identified as following:

Stabilized condensate composition tabulated in table 3 according to design document and material balance.

Table3. Stabilized Condensate Composition

Component	Mole %	Component	Mole %
H ₂ O	1.3E-06	C ₁₁ cut	4.6809
N ₂	2.15E15	C ₁₂ cut	3.2151
CO ₂	5.29E-8	C ₁₃ cut	2.6262
H ₂ S	2.08E-04	C ₁₄ cut	1.754
C ₁	5.56E-09	C ₁₅ cut	1.1652
C ₂	1.46E-04	C ₁₆ cut	0.8739
C ₃	0.243	C ₁₇ cut	0.5856
iC ₄	1.7501	C ₁₈ cut	0.5856
nC ₄	4.792	C ₁₉ cut	0.2913
iC ₅	8.2837	C ₂₀ ⁺	0.8739
nC ₅	8.4096	COS	2.04E-05
C ₆ cut	12.3037	CH ₄ S	0.0129
C ₇ cut	13.7782	ETSH	0.4497
C ₈ cut	14.955	PR1THIOL	0.4117
C ₉ cut	10.2615	BU1THIOL	0.1254
C ₁₀ cut	7.3268	HX1THIOL	0.245

Different components were present in the software data bank with the exception of mercaptan and sulfur compounds which were defined using different information and software. (See table4 for further information)

Table4. Sulfur and Mercaptan Compounds Properties

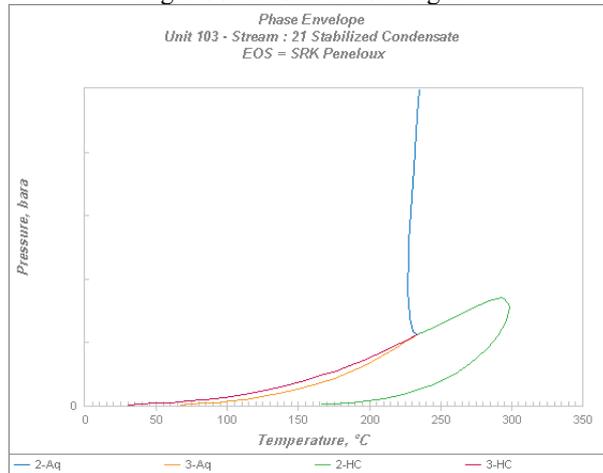
	MW	NBP	Density	Tc	Pc	Vc	ω
	-	°C	g/cm ³	°C	bara	cm ³ /mol	
COS	60.07	-50.15	1.015	105.6	6.180	142	0.1041
CH ₄ S	48.11	5.946	0.8632	196.8	7.235	145	0.155
ETSH	62.13	35.05	0.8365	225.8	5.492	207	0.190
PR1THIOL	76.15	66.05	0.8459	262.9	4.519	263	0.279
BUT1THIOL	90.19	98.46	0.8459	293.9	3.970	307	0.2784
HX1THIOL	116.2	158.8	0.9547	390.9	3.970	355	0.2641

Then, physical and chemical properties of condensate calculated at 37.1°C and 1.1 bar which were compatible with design data. Furthermore, phase diagram of this stream plotted in Fig. 1.

Table5. Physical and Chemical Properties of Condensate Calculated @ 37.1°C and 1.1 bar

	MW	Density (g/cm ³)	z	Viscosity (cp)
PVTsim	109.24	0.6474	6.70E-03	0.4470
Design	110.06	0.7232	6.20E-03	0.3862
Error %	0.7	10.1	7.7	13.6

Fig1. Condensate Phase diagram



For defining DSO stream and its main components, mainly paraffinic disulfide, HYSYS data bank was used. About 87% of DSO comprised of compounds mentioned in table 6. Chemical properties of DSO also prepared using HYSYS. (table7)

Table6. Physical properties of DSO

	MW	NBP	Density	Tc	Pc	Vc	ω
	-	°C	g/cm ³	°C	bara	cm ³ /mol	
C2H6S2	94.22	109.75	1.068	341.85	53.6	252	0.2059
C3H8S2	108.25	134	1.0249	355.75	46.15	312	0.3010
C4H10S2	122.28	153.98	0.9969	368.85	38.7	358	0.3469
C5H12S2	136.31	173.7	0.9785	386.85	36.1	417	0.391
C6H14S2	150.34	195.85	0.9645	401	30.3	463	0.437

Using required data, PVTsim software run and DSO properties got. Its phase diagram also plotted in Fig 2.

Table7. DSO characteristics

	MW	Density (g/cm ³)	Viscosity (cp)
PVTsim	120.06	1.0282	0.8434
Design	-	1.030	0.8500
Error %	-	0.19	0.8

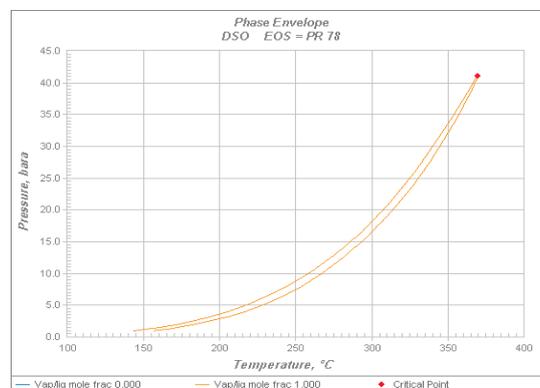


Fig2. DSO phase diagram

To study the possibility of wax formation, first different mixtures of DSO and condensate defined and then wax formation checked for specific pressure and temperature. Table8 indicates software results for three different ratios which 1:1 and 3:1 of condensate and DSO used for results validation. In addition, real ratio based on production rates also considered.

Table8. Different Mixtures Properties (1:1, 3:1, 10,000:5)

Mixing Ratio	MW	Density (g/cm ³)		Viscosity (cp)	
	-	Temperature°C			
		20	37	20	37
1:1	115.36	0.8412	0.8297	0.7693	0.6926
3:1	112.52	0.7478	0.7366	0.6589	0.5623
10000:5	109.2	0.6584	0.6475	0.5346	0.4493

Calculations @ 20 °C are in good agreement with lab results for density of two ratios, 1:1 and 3:1. PT diagram of wax formation plotted for these two ratios.

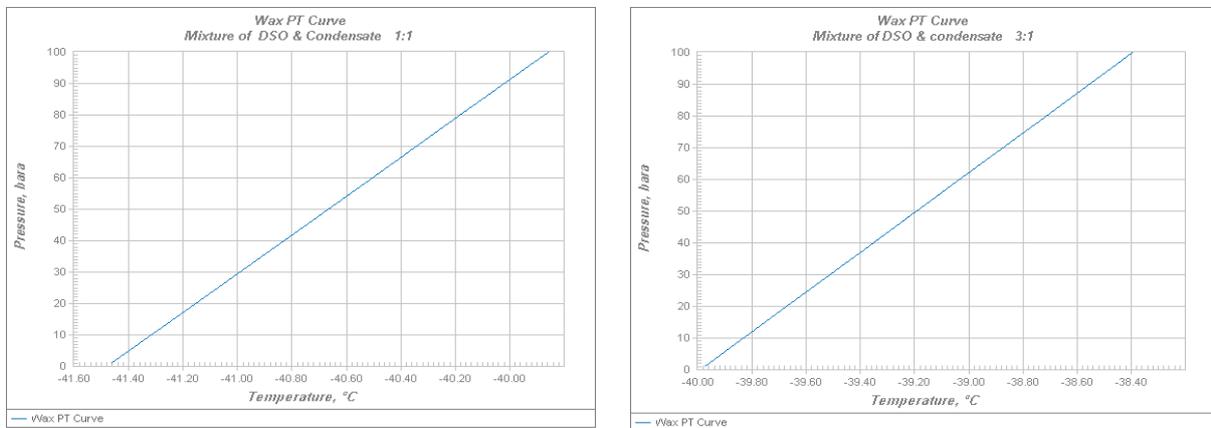


Fig3. PT Diagram of Wax Formation for Two Ratios

Weight fraction of wax at different temperature and 1 bar indicated in Fig 4.

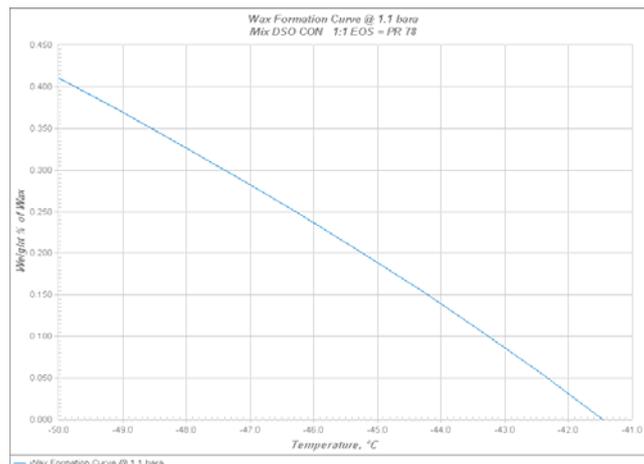


Fig4. Weight Fraction of Wax in 1bar

Fig5&6 depict required conditions and amount of wax formed while DSO and condensate mixed with each other in real conditions.

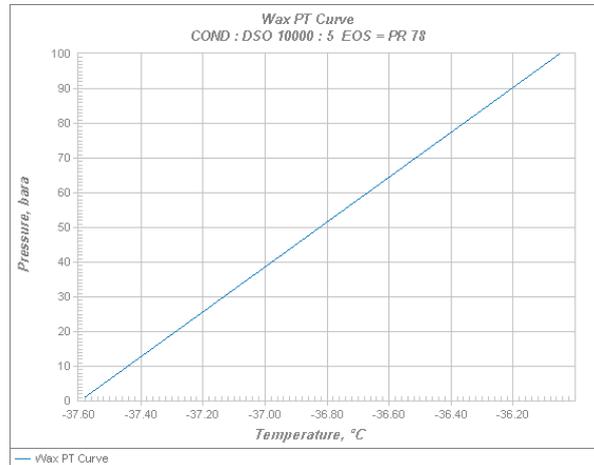


Fig5. Phase Diagram of Wax Formation for Real Ratio

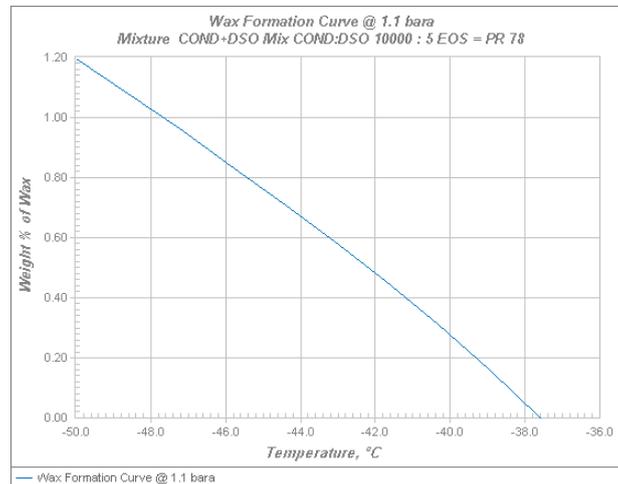


Fig6. Wax Weight Fraction for real ratio in 1 bar

Lab Tests

Distillation and wax formation possibility tests were done for different mixtures of DSO and condensate as following:

- ✓ Test1: Distillation test (ASTM D86) was done for 100ml of pure condensate, so recovery and residual % measured for this sample.
- ✓ Test2: A mixture of 0.7 ml DSO and 100 ml of pure condensate prepared and distillation test (ASTM D86) done for it.
- ✓ Test3: A mixture of 0.7 ml DSO and 99.3 ml of pure condensate prepared and distillation test (ASTM D86) done for it.
- ✓ Test4: A mixture of 0.7 ml DSO and 99.3 ml of pure condensate prepared and kept in proper place for one week, then distillation test (ASTM D86) done for it.

The test results are as below :

Test No	1	2	3	4
IBP °C	28.7	28.3	28.2	28.4
FBP °C	308	306.1	302.4	304.7
Residue (%)	2	2.1	2	2.1
Corrected Recovery (%)	95.9	97.1	96.9	96.9

Results

Tests results tabulated in table 10. In accord with these results DSO injection to condensate with 1:100 ratios in ambient conditions has no effect on heavy cuts of mixture; even it appears that DSO injection lightened the condensate.

Conclusion

1. The only way to transfer DSO to condensate storage tanks is using a connection located on DSO storage tanks. According to investigations, in real cases DSO injection can cause increase in total sulfur of condensate about 550 ppmw. In addition, different DSO pollutants such as caustic and MEROX catalyst can be source of problem.
2. According to design documents, there is no specification for total sulfur, but it seems acceptable limit for international shipping is 3000 ppmw. Valid specification should be identified by relevant disciplines.
3. Lab results indicate that DSO injection lightened the condensate.
4. Simulation results indicate that for mixture of DSO and condensate for moderate and operational pressures (1-50 bar) wax formation temperature is -37 and -41°C. In real case, wax weight fraction @ -50 °C is 1.2 %w.