

## REMOVING HYDROCARBONS FROM METHANOL-WATER MIXTURES

T. C. Frankiewicz  
Moshen Zaouk

NATCO GROUP

12<sup>th</sup> Annual Produced Water Seminar  
Houston, TX

January 2002

NATCO GROUP

## Summary

The original objective for this project was to determine means to reduce the residual hydrocarbons in a methanol/brine mixture to <30 PPM. In the course of the study, it was determined that the solubility of hydrocarbons in methanol/brine at 80°F is about 40 - 45 PPM if measured by EPA 413.1 (Gravimetric). However, if measured by EPA 413.3 (Infrared) or by gas chromatography/mass spectroscopy (GC/MS), the solubility is, in reality, 440 to 460 PPM. 80% of the soluble hydrocarbons are volatile and thus lost when a gravimetric analytical procedure is used. Thus reducing the total hydrocarbons to <30 PPM will require the use of an adsorbent material.

The time required for the bulk separation of methanol/brine and condensate is about 5 minutes. The required separation time is not affected by the presence of the corrosion inhibitor or scale inhibitor expected to be used on this platform.

Due to the formation of a very tight reverse emulsion with very small (2 - 10 micron) condensate droplets in the methanol/brine, neither hydrocyclones nor coalescing beds of garnet or walnut shells were effective at reducing the dispersed hydrocarbons to <50 PPM. Water treated by these means retained a hazy appearance. At 80°F, a hydrocyclone was ineffective at reducing the level of dispersed hydrocarbons in the methanol/brine.

NATCO GROUP

## Summary (Continued)

A coalescing filter was effective at increasing the droplet sizes of condensate dispersed in the methanol/brine, producing crystal clear fluid with residual condensate dispersed as moderately sized droplets. The coalescing filter consistently effected the removal of 80 to 90% of the dispersed hydrocarbons. Two stages of coalescence should thus remove 96 to 99% of the dispersed hydrocarbons.

A commercially available modified clay adsorbent was tested for its ability to remove dispersed and dissolved hydrocarbons from methanol/brine. The adsorbent reduced the residual hydrocarbons in the methanol/brine to <1 PPM as measured by EPA 413.1. Because the concentration of dissolved hydrocarbons to be recovered is high, however, this technology would place an economic burden on the water treatment process systems.

The recommended means for removing dispersed hydrocarbons from the methanol brine consists of a desanding hydrocyclone to remove solids, followed by a 2-phase flash separator vessel to keep excessive gas out of the coalescer filters. From the flash vessel, the methanol/brine would be fed to twin, specially designed coalescer vessels that can be operated individually, together, in parallel, or in series.

NATCO GROUP

## Project Objectives

- Characterize the "representative" condensate used in the study for future comparison against actual produced condensate
- Define the chemical and physical parameters that affect the ability to separate condensate from methanol-water (MeOH-Wtr) mixtures
- Identify viable technology for the efficient separation of dispersed and dissolved hydrocarbons from MeOH-Wtr mixtures

NATCO GROUP

## Condensate Characterization

- Synthetic Condensate
  - N-Heptane 20%
  - Diesel Fuel 5%
  - Kerosene 75%
- Gulf of Mexico Condensate
  - 49° API
  - PONA Analysis
    - Paraffinic 64%
    - Olefinic 2%
    - Naphthenic 23%
    - Aromatic 11%

WATGOSOURCE

## Condensate Characterization

- Gulf of Mexico Condensate
  - BTEX content 7.7%
  - Density 0.79 @ 60°F
  - Viscosity 1.9 cP @ 60°F
  - Viscosity 0.7 cP @ 120°F
  - Cloud Point 62° F
- Other Analyses:
  - Geochem Fingerprint GC analysis up to C<sub>30</sub>
  - Simulated Distillation by GC

WATGOSOURCE

## Aqueous Phase Characterization

- Mixture: 60% water and 40% methanol
  - Brine Composition
    - CaCl<sub>2</sub> 2000 mg/liter
    - MgCl<sub>2</sub> 2000 mg/liter
    - NaCl 8000 mg/liter
  - Note: CaSO<sub>4</sub> precipitate forms in MeOH-Water phase
  - Liq. - Liq. Interfacial Tension: 16.5 dynes/cm @ 90°F
- | Temp. | Viscosity | Density    |
|-------|-----------|------------|
| 49°F  | 2.1 cP    | 0.914 g/cc |
| 122   | 0.8       | 0.884      |

WATGOSOURCE

## Physical and Chemical Parameters Impacting MeOH-Wtr and Hydrocarbon Separation

- Liquid - Liquid Interfacial Tension
  - Stabilizes small oil droplets
  - Limits effectiveness of hydrocyclones and coalescing media
- Relatively small gravity differential between liquid phases
  - Limits effectiveness of any gravity based separation
- Relatively high viscosity of aqueous phase
  - Reduces hydrocyclone efficiency
  - Slows any gravity based separation

WATGOSOURCE

### Physical and Chemical Parameters Impacting MeOH-Wtr and Hydrocarbon Separation

- Aromatic/polar content of hydrocarbon phase
  - Increased soluble hydrocarbons in aqueous phase
- Cloud point of hydrocarbon phase
  - Wax precipitation can stabilize emulsions, inhibit droplet coalescence
- Presence of sulfate in aqueous phase
  - Sulfate salt precipitation stabilizes emulsions, can clog coalescing beds or media
- Scale/Corrosion inhibitor(s) or other chemicals

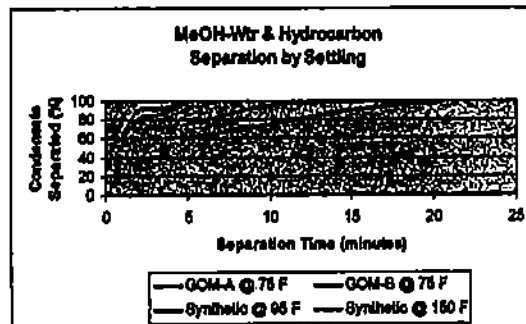
NAI GROUP

### Technology for Separating Hydrocarbons from MeOH Mixtures

- Gravity based separation
  - Residence Time
  - Hydrocyclones (liquid/liquid and solid/liquid)
  - Centrifuging
- Coalescence
  - Coalescing bed
  - Filter-coalescer
  - Chemical treatment (floculants, reverse demulsifiers)
- Adsorption of soluble hydrocarbons

NAI GROUP

### Gravity-based Hydrocarbon Separation Rates were Variable



NAI GROUP

### Residual Hydrocarbons in MeOH-Wtr after 30 minutes of settling (EPA 413.1, Gravimetric)

Condensate	Temperature	Residual Hydrocarbons
GOM-A	75° F	1015 PPM
GOM-B	75	1140
Synthetic	95	870
Synthetic	150	1100

Data indicate the presence of a relatively stable reverse emulsion after bulk separation.

NAI GROUP

**Solubility of Hydrocarbons in MeOH-Wtr  
Mixture as Determined by  
Three Analytical Methods**

Condensate	Analysis	Soluble HC's. mg/liter		
		50°F	100°F	150°F
Synthetic	413.1	-	49	67
GOM	413.1	42	53	50
GOM	413.2	490	610	690
GOM	GC/MS	440	550	700

80% of soluble hydrocarbons are aromatic  
16% of soluble hydrocarbons are C<sub>2</sub> - C<sub>11</sub> aliphatics

WATSON

**Hydrocyclone Separation was  
Poor at Low Temperatures**

Fluid Temp	Hydrocyclone Pressure Drop		Hydrocarbons	
	Inlet - Underflow	Inlet - Reject	Inlet	Underflow
<u>Hydrawid LQ Decolting Hydrocyclone</u>				
55 F	25 psig	50 psig	1081	1069
			1384	1361
84 F	20	40	890	252
114 F	15	30	805	178
<u>FluChamp 1" Desanding Hydrocyclone</u>				
88 F	15	30	1205	183
116 F	18	30	1340	162

Note: Analyses by EPA 413.1, gravimetric.  
Hydrocyclone product liquid remained hazy in appearance

WATSON

**Deep Bed Coalescence was not Effective  
for MeOH-Wtr / Hydrocarbon Separation**

Fluid Temp.	Coalescing Media	Hydrocarbons	
		Inlet	Underflow
88°F	Garnett	641	237
	Walnut Shell	711	261
115°F	Garnett	550	250
	Walnut Shell	677	232

NOTE: Outlet water settled for 5 min. prior to analysis  
Analyses by EPA 413.1, gravimetric  
Product water retained a visible haze  
38 GPM/ft<sup>2</sup> flux through 24" bed depth

WATSON

**A coalescing filter element successfully  
clarified MeOH-Wtr Phase**

Flow	Cl + Sl	Inlet	Outlet
2 GPM	No	1661 PPM	79 PPM
2	Yes	1444	73 - 125
2	Yes	634	145
4	No	653	126

Note: Fluid Temperature: 54 ± 4°F  
Product water visually clear  
Analyses by EPA 413.1, gravimetric

WATSON

**Product Water from Hydrocyclone and Coalescing Beds Remained Cloudy. Coalescing Filter Produced Clear Water**



WATGOSOURCE

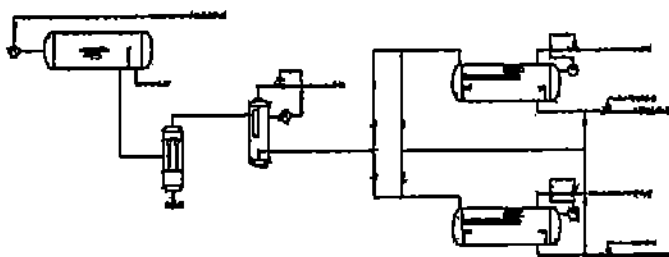
**Process Issues for Coalescing Filters in MeOH-Wtr & Hydrocarbon Separation**

- Wax formation at low process temperatures can blind coalescer
  - Resolution: operate above cloud point
- Sulfate salt precipitates can plug coalescer element
  - Resolution: inject effective scale inhibitor
- Formation solids can plug coalescer element
  - Resolution: remove with hydrocyclone or pre-filter
- Premature release of condensate droplets from fibers in coalescer elements
  - Resolution: operate twin coalescers in series

WATGOSOURCE

**Process Flow Diagram for Coalescence & Removal of Hydrocarbons from MeOH-Brine Mixtures**

L.P. Separator    Demisting Hydrocyclone    Demisting Drum With/Without Tube Inlet    Condensate Collector Vessels



WATGOSOURCE

**An Organophilic Clay showed Good Activity for Removing Hydrocarbons from MeOH-Wtr Mixtures**

Aquatech ET-1 adsorbent bed volume: 1100 ml  
 Process Flow Rate: 110 ml/min

Test	Feed	ET-1 Product	GAC Product
1	1410 PPM	216 PPM	100 PPM
2	705	79	-
3	78	<1	<1
4	190	<1	<1
	115	10	<1

Note: 21 bed volumes of water processed.  
 Estimated bed loading at conclusion of test is 3% hydrocarbons by wt.  
 Analyses by EPA 413.1, gravimetric

WATGOSOURCE

## Conclusions

- Condensate tends to form a tight reverse emulsion in MeOH-Wtr mixtures
- Hydrocarbon solubility in MeOH-Wtr mixtures is temperature dependent
  - 500 – 1000 PPM, depending upon temperature
- Low process temperature is preferred to limit the concentration of dissolved hydrocarbons

WALCO GROUP

## Conclusions (Continued)

- Time, coalescing beds, and hydrocyclones were unable to produce a clarified MeOH-Wtr mixture at a low process temperature
- A coalescing filter successfully removed dispersed hydrocarbons from the MeOH-Wtr mixture
- An organophilic clay adsorbent was able to remove dissolved hydrocarbons from the MeOH-Wtr mixture

WALCO GROUP

## Acknowledgement

We wish to express our thanks and appreciation to the  
Williams Field Service Company  
and to  
Mel Wood  
Project Manager for the  
Canyon Express Project  
for permission to present the  
material in this paper

WALCO GROUP