Study of a waxy crude oil crystallization under pressure: 
DSC and rheological analysis 
(Étude de la cristallisation sous pression d’un brut paraffinique : Analyses calorimétriques et rhéologiques)

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AGENDA

Introduction

- Paraffinic crude oils and wax crystals
- Industrial challenges

Influence of pressure on crystallization

- Wax Appearance Temperature (WAT) - DSC
- Flow properties - Rheology

Relationship between yield stress and wax crystals content at the onset of gelation
Waxy crude oils: the rheological behavior

T > WAT
Newtonian liquid
Low viscosity

T < WAT
Non Newtonian fluid
Yield stress
Shear thinning
Paraffinic crude oils: wax crystals

- Long chains of n-paraffins form spherulites at low temperature (T < WAT)
  → spherulites size depending on the cooling rate

I. Hénaut, O. Vincké, F. Brucy
Industrial challenges

Wall deposit in flow lines

Pipeline plugging and restartability
- What restart pressure?
- How long does it take?

→ Strongly related to the initial structure of the way gel

http://mansoori.people.uic.edu/Wax.and.Waxy.Crude_html
http://nfatmala.blogspot.fr/2016/02/hydratexasphalt-in-subsea-pipeline.html
Impact of pressure on WAT: literature review

- Dead oil (no dissolved gas)
  - Increase of WAT (about 2°C per 100 bar)

- Live oil (with dissolved gas)
  - Decrease of WAT until saturation and then increase of WAT

INFLUENCE OF PRESSURE ON CRYSTALLIZATION

**Impact of pressure on WAT**

HP µ DSC-VII from SETARAM

Experimental procedure:
Initial heating from 20 to 80°C at 2°C/min,
Thermal peak hold at 80°C during 2 hours,
Cooling from 80 to -40°C at -1°C/min
Peak hold at -40°C during 5 minutes,
Heating back to 80°C at 2°C/min.
Impact of pressure on WAT: DSC results (from 1 to 90 bar)

Slight increase of WAT with pressure
INFLUENCE OF PRESSURE ON CRYSTALLIZATION

Impact of pressure on crystallized paraffin content

$$X_T(\%) = \frac{\Delta H(T)}{\Delta H_{\text{total}}}$$

Crystallized paraffin content $X_T(\%)$ in function of temperature and pressure

- Increase of solid wax content with decreasing temperature
- Increase of solid wax content with pressure
Impact of pressure on viscosity: literature review


Increase of viscosity with pressure
INFLUENCE OF PRESSURE ON RHEOLOGY

Impact of pressure on viscosity and yield stress

Pressure cell of a rheometer + conical geometry

Experimental procedure:
Initial heating at 60°C,
Cooling from 60°C to 30°C at -1°C/min,
- Dynamic cooling (200s⁻¹) → viscosity measurement
- Static cooling → oscillatory measurements (G’) and flow curve at T_{finale}
INFLUENCE OF PRESSURE ON RHEOLOGY

Impact of pressure on “rheological WAT”

Impact of temperature and pressure on viscosity during a dynamic cooling (200s⁻¹)

Impact of temperature and pressure on elastic modulus $G'$ during a static cooling

Increase of “rheological WAT” with pressure
INFLUENCE OF PRESSURE ON RHEOLOGY

- Impact of pressure on yield stress
  - Static cooling from 60°C to $T_f$ + flow curves at $T_f$ at -1°C/min
  - Yield stresses determined by zero shear rate extrapolation from a flow curve

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<th>P(atm)</th>
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Impact of temperature and pressure on yield stress after a static cooling

- Increase of yield stress with decreasing temperature
- Increase of yield stress with pressure
Relate the solid wax content to the yield stress value.

\[ \tau_y(\chi_T, T, P) + \tau_y(T, P) \]

Impact of solid wax content on yield stress.

Strong link between yield stress and wax crystals: the amount of crystals balances the impacts of pressure and temperature (around onset of crystallization).
CONCLUSIONS AND PERSPECTIVES

Conclusions

- Impact of pressure on WAT and rheological properties of a gelled waxy crude oil
- DSC + Rheometry → link between wax crystals and yield stress aside from pressure and temperature (around the onset of crystallization)

Future works

- Enlarge temperature conditions going to lower temperature from WAT
- Evaluate the impact of the paraffin distribution on $\tau_{\gamma}(X_T)$
  - Perform these analysis with dissolved gas
  - Perform these analysis on other waxy crude oils
Innover les énergies

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