Cristallisation isotherme des bruts paraffiniques

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Agenda

- Basics on waxy crude oils rheology
  - Main features
  - Characterization challenges
- Aging phenomenon and isothermal crystallization
  - Definition
  - Rheological and DSC results
- Conclusion
Basics on waxy crude oils rheology

- Main features: typical flow curves

- Increase in viscosity and shear thinning behavior
- Yield stress
Basics on waxy crude oils rheology

- Main features: typical oscillatory curves

Increase in solid like behavior ($G'>G''$)
Basics on waxy crude oils rheology

- Characterization challenges: versatility of properties

- Change of morphology upon cooling rate

- Change of rheology upon cooling conditions

![Image of morphology change](image1.png)

![Graph showing rheology change](image2.png)
Aging phenomenon and isothermal crystallization

- **Definition**: Increase of elastic modulus during an holding time at constante temperature

Appearance of additional crystals?

Re-organisation of existing crystals (Oswald Ripening)?

Delay of thermal diffusion?

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J.A. Lopes da Silva and J.A.P. Coutinho

‘Analysis of the isothermal structural development in waxy crude oils under quiescent conditions’

Energy&Fuels, 2007, 21, 3612-3617
Aging phenomenon and isothermal crystallization

- Experimental approach: DSC and rheological measurements

Mettler Toledo DSC1 and 40μl cell.

AR2000 Rheometer TA Instruments
Aging phenomenon and isothermal crystallization

- Preliminary rheological characterization: cooling under shear (-5°C/min)

![Graph showing the relationship between temperature and viscosity with WAT approximately 40°C.](image)

- $T < \text{WAT}$: High viscosity and shear thinning behavior
- $T > \text{WAT}$: Low viscosity and newtonian behavior

WAT $\approx 40°C$
Aging phenomenon and isothermal crystallization

- Preliminary rheological characterization: cooling under shear
- Influence of cooling rate

- On final viscosity
- On final elastic modulus after cooling at 50s\(^{-1}\)

For samples cooled under shear, viscosity and elastic modulus increase with cooling rate.
Aging phenomenon and isothermal crystallization

- Preliminary rheological characterization: quiescent cooling
- Influence of cooling rate on final elastic modulus

For samples statically cooled, elastic modulus decreases with cooling rate.
Aging phenomenon and isothermal crystallization

- evolution of $G'$ with time: samples statically cooled

-1°C/min

-10°C/min

No aging
Aging phenomenon and isothermal crystallization

- Evolution of $G'$ with time: samples statically cooled
Aging phenomenon and isothermal crystallization

- Evolution of $G'$ with time: samples statically cooled

![Graph showing the evolution of $G'$ with cooling rate.](image)
Aging phenomenon and isothermal crystallization

- evolution of $G'$ with time: samples statically cooled

![Graph showing the evolution of $G'$ with cooling rate](image)
Aging phenomenon and isothermal crystallization

- evolution of $G'$ with time: samples statically cooled
Aging phenomenon and isothermal crystallization

- evolution of $G'$ with time: samples statically cooled and cooled under shear
Aging phenomenon and isothermal cristallization

- Evolution of $G'$ with time: samples cooled under shear
- Holding time at rest
Aging phenomenon and isothermal crystallization

- evolution of $G'$ with time: samples cooled under shear
- Holding time at rest
Aging phenomenon and isothermal crystallization

- Evolution of $G'$ with time: samples cooled under shear
- Holding time at rest
Aging phenomenon and isothermal crystallization

- Evolution of $G'$ with time: samples cooled under shear
- Holding time at rest
Aging phenomenon and isothermal crystallization

- **DSC results**
  - 60°C to 30°C with various cooling rates (-0.25° to 30°C/min)
  - Heat exchanged during isothermal crystallization from 60 to 30°C
Aging phenomenon and isothermal cristallization

- DSC results of subsequent isothermal steps
- 2 crude oils (WAT of S = 40°C WAT of D = 20°C) same Cp

- Isothermal heat flow at 45°C
- Isothermal heat flow at 30°C

\[ \frac{dQ}{dt} = cp \frac{dT}{dt} \]

\[ \frac{dQ}{dt} = cp \frac{dT}{dt} + \text{thermal event} \]
Aging phenomenon and isothermal crystallization

- DSC results: total exchanged heat vs anisothermal heat
Conclusion

- Aging is favored by
  - High cooling rate at quiescent conditions
  - No aging after slow dynamic cooling (beneficial effect)

- Isothermal crystallization is fast

- Slow evolution ≠ isothermal crystallization
  - Thermal delay (high volume)
  - Structural change (Ostwald ripening, molecular diffusion)
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🐦 @IFPENinnovation
Aging phenomenon and isothermal crystallization

- evolution of $G'$ with time: samples statically cooled

$-10^\circ C/min$