

EVALUATION OF THIXOTROPIC MODELS FOR WAXY CRUDE OILS BASED ON SHEAR STRESS DECAY AT CONSTANT SHEAR RATES

JINJUN ZHANG^{1*}, LIPING GUO^{1,2}, HOUXING TENG¹

¹ The MOE Key Laboratory of Petroleum Engineering/Beijing Key Laboratory of Urban Oil and Gas Distribution Technology, China University of Petroleum, Beijing 102249, China

² College of Petroleum Engineering, Daqing Petroleum Institute, Daqing 163318, China

* Email: zhangjj@cup.edu.cn

Fax: x86.10.89734627

Received: 10.8.2009, Final version: 10.12.2009

ABSTRACT:

Thixotropy is an important rheological behavior of waxy crude oils. The objective of this paper is to demonstrate existing model's abilities to describe shear stress decay behaviors of waxy crude oils at constant shear rates. Seven models specially developed for or currently used to waxy crude oils are reviewed as well as two viscoelastic-thixotropic models for human blood. Stress decay behaviors were measured for four waxy crude oils and at various temperatures. Each of the models was used to fit the stress decay plots at a single shear rate, and at multiple shear rates, respectively. Globally, Zhao's model, a complex viscoplastic model with two structure parameters and twelve physical & fitting parameters, matched the experimental plots better than other compared models. While the three models with viscoelastic backgrounds were not quite successful. For use of models, one may make choice by comprehensively considering a model's complexity in mathematic form and abilities to describe the rheological behaviors.

ZUSAMMENFASSUNG:

Thixotropie stellt eine wichtige Eigenschaft wachsartiger Erdöle dar. Das Ziel dieses Artikels ist zu zeigen, dass existierende Modelle für wachsartige Erdöle den Abfall der Scherspannung bei konstanter Schergeschwindigkeit beschreiben können. Sieben Modelle, die eigens für wachsartige Erdöle entwickelt worden sind, und zwei weitere viskoelastisch-thixotrope Modelle für menschliches Blut werden in dieser Arbeit betrachtet. Der Spannungsabfall wurde für vier wachsartige Öle bei verschiedenen Temperaturen gemessen. Jedes dieser Modelle wurde angewandt, um den Spannungsabfall bei einer einzelnen bzw. mehreren Scherraten zu fitten. Das Modell von Zhao, ein komplexes viskoplastisches Modell mit zwei Strukturparametern und zwölf physikalischen und Fitparametern, beschrieben die experimentellen Daten besser als die anderen Modelle, während die drei Modelle, die auf Viskoelastizität basieren, nicht erfolgreich waren. Bei der Anwendung der Modelle kann man zwischen der mathematischen Komplexität und der Fähigkeit wählen, das rheologische Verhalten zu beschreiben.

RÉSUMÉ:

La thixotropie est un comportement rhéologique important du brut paraffineux. L'objectif de cet article est de démontrer les capacités de modèles thixotropiques existents pour décrire le gradient de contraintes de cisaillement du brut paraffineux en constante vitesse de cisaillement. Sept modèles thixotropiques actuellement utilisés dans le brut paraffineux sont discutés ainsi que deux modèles viscoélastique-thixotropique pour le sang humain. Visant les quatre bruts paraffineux, la relaxation de contraintes de cisaillement est mesurée par expérimentation sous les températures variées. Chaque de ces modèles mentionnés sont utilisés pour l'ajustement des données de gradient de vitesse de cisaillement respectivement sous la vitesse unitaire de cisaillement et de multiples vitesses de cisaillement. Globalement, le modèle viscoplastique complexe de Zhao avec deux paramètres de structure et douze paramètres d'ajustement s'assortent mieux aux données expérimentales que les autres modèles. L'effet des trois modèles viscoélastiques n'est pas très idéal. Pendant l'application de ces modèles, on peut faire son choix tout en considérant la complexité mathématique et les capacités de la description du comportement rhéologique.

KEY WORDS: waxy crude oil, thixotropy, shear stress decay, model, evaluation

Oil	Shear rate [1/s]	Average AADs of various model [%]								
		Houska	Zhao	Chen	Hou	Liu	Fang-1	Fang-2	Cast-1	Cast-2
1	1	5.3	0.9	4.1	0.6	11.4	8.9	10.8	12.6	5.8
	2	6.9	1.0	2.7	0.3	12.9	13.3	13.1	13.2	4.6
	4	9.4	1.4	2.7	0.8	9.7	8.8	8.3	12.2	4.5
	8	11.0	3.0	1.0	0.9	10.0	10.2	7.2	11.6	6.4
	average	8.1	1.6	2.6	0.6	11.0	10.3	9.8	12.4	5.3
2	1	5.1	0.8	3.2	0.5	9.2	9.1	9.3	10.1	3.8
	2	7.6	0.9	3.3	0.3	10.4	10.8	10.5	11.2	4.3
	4	10.7	2.5	2.5	0.6	10.9	10.8	10.9	10.3	5.7
	8	9.3	2.4	2.2	0.7	10.8	7.0	4.3	9.4	6.3
	average	8.2	1.7	2.8	0.5	10.3	9.4	8.8	10.35	5.0
3	1	2.9	0.6	1.6	0.5	9.7	6.9	9.2	11.1	3.5
	2	2.3	0.5	1.4	0.4	10.2	5.9	8.2	10.6	3.8
	4	3.6	0.4	1.6	0.3	8.7	6.7	10.4	9.4	3.4
	8	5.6	0.7	1.6	0.1	7.0	6.4	8.0	7.8	3.1
	average	3.6	0.6	1.6	0.3	8.9	6.5	8.9	9.8	3.5
4	1	4.7	1.0	3.4	0.8	8.1	3.9	3.9	8.7	3.4
	2	9.1	1.8	2.8	0.6	9.2	8.9	9.2	9.3	4.4
	4	6.0	1.7	2.4	0.2	6.7	4.5	4.0	7.2	3.3
	8	4.5	1.3	1.5	0.8	4.7	4.2	3.5	5.1	2.5
	average	6.1	1.4	2.5	0.8	7.2	5.4	5.1	7.6	3.4
overall average	6.5	1.3	2.4	0.6	9.3	7.9	8.2	10.0	4.3	

Oil	Temperature [°C]	Average AADs of various model [%]								
		Houska	Zhao	Chen	Hou	Liu	Fang-1	Fang-2	Cast-1	Cast-2
1	32	15.9	3.8	12.0	12.2	20.9	23.9	16.1	21.4	14.9
	33	12.4	3.6	11.1	8.8	18.3	19.1	12.6	20.4	14.5
	34	8.1	2.6	5.0	7.2	15.1	13.7	8.1	13.4	9.2
	35	5.2	2.4	3.5	5.2	13.3	12.5	5.3	13.4	9.8
	36	4.6	1.6	2.1	4.0	6.3	6.5	4.0	7.8	5.9
	average	9.3	2.8	6.7	7.5	14.8	15.1	9.2	15.3	10.8
2	32	13.6	3.2	5.0	10.4	16.8	16.0	13.8	22.8	17.4
	33	11.9	3.4	7.9	9.8	15.3	14.9	11.8	22.2	17.1
	34	11.3	4.0	9.0	8.7	16.8	15.2	11.9	20.2	15.7
	35	7.1	3.3	4.0	6.0	12.2	12.0	6.8	17.8	14.2
	36	5.3	2.4	3.6	5.9	10.9	9.9	5.8	14.5	11.2
	average	9.8	3.3	5.9	8.1	14.4	13.6	10.0	19.5	15.1
3	38	10.6	1.8	2.5	5.6	19.3	13.9	10.9	16.9	12.3
	39	9.8	2.7	5.8	6.6	17.9	12.4	11.6	15.7	12.0
	40	7.3	5.0	6.3	7.1	12.8	10.6	8.3	12.7	9.2
	average	9.2	3.2	4.9	6.4	16.7	12.3	10.3	15.1	11.2
4	28	14.1	4.3	4.2	9.9	17.4	19.9	14.1	23.4	17.5
	29	13.4	3.3	3.5	11.7	18.5	16.1	13.4	22.4	17.1
	30	9.7	3.2	5.1	7.4	14.8	13.9	9.8	21.0	16.5
	31	7.3	3.3	4.5	7.0	13.0	11.0	7.5	17.3	13.6
	32	5.8	3.3	3.7	5.8	10.1	8.5	6.8	14.3	11.1
	average	10.1	3.5	4.2	8.4	14.8	13.9	10.3	19.7	15.2
	overall average	6.5	1.3	2.4	0.6	9.3	7.9	8.2	10.0	4.3

Table 2 (above):
The average absolute deviations of fittings to single shear rate data.

Table 3:
The average absolute deviations of fittings to multiple shear rate data.

4 CONCLUDING REMARKS

Thixotropic models for waxy crude oils are reviewed. By using experimental data of four waxy crude oils at various temperatures, nine models are evaluated for their abilities to match shear stress decay data at constant shear rates. It is found that all studied models may fairly predict the shear stress decay behaviors if fittings are made on single shear rate basis. However, if fittings are made on multiple shear rates basis, deviations understandably become larger. This paper provides information of every model's abilities to describe shear stress decay behavior at constant shear rate. Among all studied models, Zhao's model undoubtedly shows exceptional abilities to match the shear stress decay data for all four oils and at all test temperatures even in the case of multiple shear rate fittings.

However, Zhao's model is more complicated than the currently-used Houska model that is already thought to be too much complex. Therefore, from practical point of view, if a thixotropic model is required, say, for numerical simulation of the transient flow of the thixotropic waxy

generally doubled or even more, with more than half of them above 10% and some even above 20%. Besides, the AADs show clear tendency of increase with decreasing temperature. This indicates that change of oil temperature indeed impacts model's abilities to match experimental data. However, it is in this case that Zhao's model undoubtedly shows exceptional abilities to describe the shear stress decay behaviors for all four oils and at all test temperatures, with a maximum of average AAD of only 5%.

crude oil, one may choose a less complex but acceptably accurate model. In other words, development of thixotropic models with simpler mathematic form but better accuracy is remained to be a task for future studies. Besides, the three models with viscoelastic background are found not to be quite successful in describing the shear stress decay of waxy crude oils at constant shear rates, indicating that further studies are necessary to develop viscoelastic-thixotropic models that may better characterize the thixotropic behaviors from rheological point of view. Finally, many other materials such as cement pastes [28, 29] and sludge [30] may also exhibit thixotropic behaviors. Therefore, thixotropic models developed for waxy crude oils may be considered for their fitness to these materials as well.

ACKNOWLEDGEMENTS

Supports from the National High-tech R&D Program of China (No.2006AA09Z357) and Research Project for Supervisors of Beijing Excellent PhD Dissertations (YB20081141401) as well as the National Natural Science Foundation of China (50944030) are greatly acknowledged.

REFERENCES

- [1] Vinaya G, Wachsa A, Frigaard I: Start-up transients and efficient computation of isothermal waxy crude oil flows. *J. Non-Newtonian Fluid Mech.* 143 (2007) 141–156.
- [2] Chang C, Boger DV, Nguyen QD: Influence of thermal history on the waxy structure of statically cooled waxy crude oil. *Soc. Petroleum Eng. J.* 5 (2000) 148–157.
- [3] Wardhaugh LT, Boger DV: Flow characteristics of waxy crude oils: application to pipeline design. *AIChE J.* 37 (1991) 871–885
- [4] Wardhaugh LT, Boger DV: The measurement and description of the yielding behavior of waxy crude oil. *J. Rheol.* 35 (1991) 1121–1156
- [5] Rønningsen HP. Rheological behaviour of gelled, waxy North Sea crude oils. *J. of Petroleum Sci. Eng.* 7 (1992) 177–213
- [6] Lopes-Da-Silva JA, Coutinho JAP: Dynamic rheological analysis of the gelation behavior of waxy crude oils. *Rheol. Acta* 43 (2004) 433–441.
- [7] Visintin RF, Lapasin R, Vignati E, D'Antona P, Lockhart TP: Rheological behavior and structural interpretation of waxy crude oil gels. *Langmuir* 21 (2005) 6240–6249.
- [8] Lee HS, Singh P, Thomason WH, Fogler HS: Waxy oil gel breaking mechanism: adhesive versus

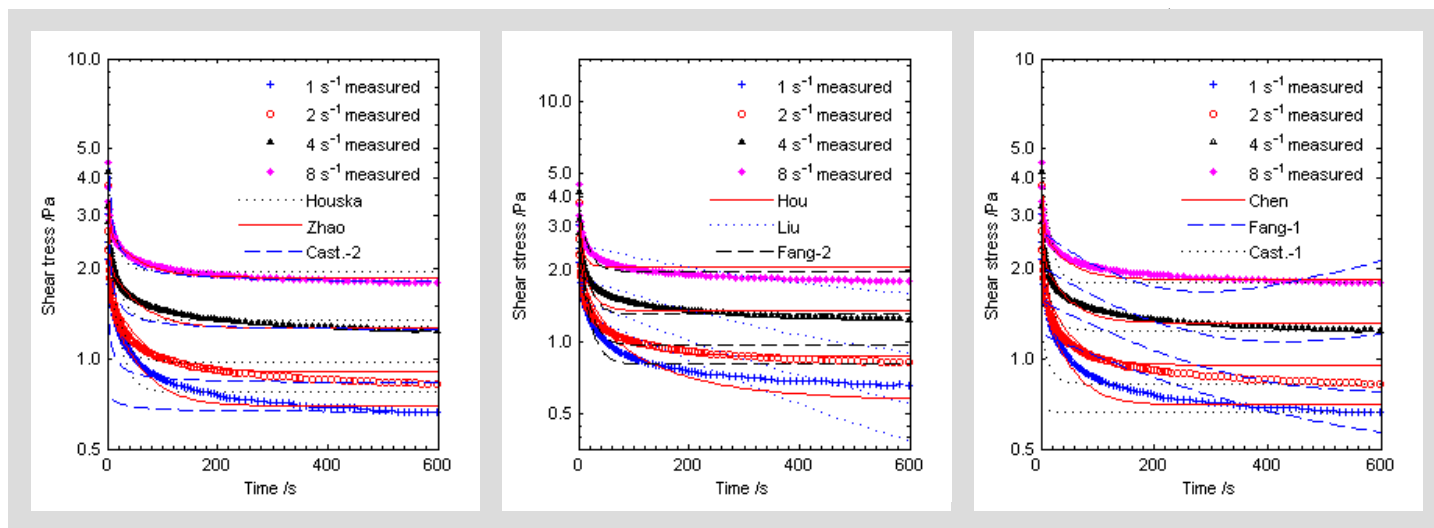


Figure 4:
Fittings of models to measured data for oil 4 at 31°C.

cohesive failure. *Energy & Fuel* 22 (2008) 480–487.

[9] Kanè M, Djabourov M, Volle JL: Rheology and structure of waxy crude oils in quiescent and under shearing conditions. *Fuel* 83 (2004) 1591–1605.

[10] Gao P, Zhang JJ, Ma GX: Direct image-based fractal characterization of morphologies and structures of wax crystals in waxy crude oils. *J. Physics: Cond. Matter* 18 (2006) 11487–11506.

[11] Ding JL, Zhang JJ, Li Hy, Zhang F, Yang XJ: Flow behavior of Daqing waxy crude oil under simulated pipelining conditions. *Energy & Fuel* 20 (2006) 2531–2536

[12] Holder GA, Winkler J: Wax crystallization from distillate fuels. *J. Inst. Pet.* 51 (1965) 228–252.

[13] Lètoffè JM, Claudy P, Kok MV, Garcin M, Volle JL: Crude oils: characterization of waxes precipitated on cooling by d.s.c. and thermomicroscopy. *Fuel* 74 (1995) 810–817.

[14] Li HY, Zhang JJ, Yan DF. Correlations between the pour point/gel point and the amount of precipitated wax for waxy crudes. *Petroleum Sci. Technol.* 23 (2005) 1313–1322.

[15] Houska M: Engineering aspects of the rheology of thixotropic liquids, Ph.D. Thesis, Czech Technical University of Prague, Prague (1981).

[16] Wachs A, Vinay G, Frigaard I: A 1.5D numerical model for the start up of weakly compressible flow of a viscoplastic and thixotropic fluid in pipelines, *J. Non-Newtonian Fluid Mech.* 159 (2009) 81–94

[17] Cawkwell MG, Charles ME: An improved model for start-up of pipelines contained gelled crude oil. *J Pipelines* 7 (1987) 41–52.

[18] Cheng DCH: Yield stress: a time dependent property and how to measure it. *Rheol. Acta* 25 (1986) 542–554.

[19] Zhao XD: Study on the unsteady hydraulic and thermal computation of the restart process of pipelines transporting PPD-beneficiated crude oil. M.Sc. Thesis, China University of Petroleum, Beijing (1999).

[20] Chen HJ: Study on restart pressure of crude oil pipeline, M.Sc. Thesis, China University of Petroleum, Beijing (2002).

[21] Hou L, Zhang JJ: Study on thixotropy of waxy crude based on viscoelasticity analysis, *J. China University of Petroleum* 29 (2005) 84–94 .

[22] Liu G, Zhang GZ, Deng Y: Viscoelasticity-thixotropy constitutive equation for gelled crude oil. *J. University of Petroleum* 27 (2003) 72–75.

[23] Castellan GW. *Physical Chemistry*. Addison-Wesley, Reading, USA (1971) 725–739

[24] Barnes HA, Hutton JH, Walters K: *An Introduction to Rheology*, Elsevier, Amsterdam (1989).

[25] Cheng DCH: Thixotropy. *Inter. J. Cosmetic Sci.* 9 (1987) 151–191.

[26] Fang B, Jiang TQ: Mathematical characterization of blood viscoelasticity and thixotropy - studies on the novel 5-parameter time-dependent constitutive equation and its suitability, *J. East China University Sci. Technol.* 24 (1998) 393–398.

[27] Fang B, Song DY, Jiang TQ: Study on the novel 7-parameter constitutive equation for viscoelastic-thixotropic fluids. *Proceedings of the Sixth National Conference on Rheology*, Wuhan, China (1999).

[28] Bouras R, Chaouche M, Kaci S: Influence of Viscosity-Modifying Admixtures on the Thixotropic Behaviour of Cement Pastes, *Appl. Rheol.* 18 (2008) 45604.

[29] Jarny S, Roussel N, LeRoy R, Coussot P: Thixotropic behavior of fresh cement pastes from inclined plane flow measurements, *Appl. Rheol.* 18 (2008) 14251.

[30] Baudez J-C: Physical aging and thixotropy in sludge rheology, *Appl. Rheol.* 18 (2008) 13495.

