Journal of Thermal Analysis and Calorimetry, Vol. 85 (2006) 1, 31–36

THERMAL AND RHEOLOGICAL STUDY OF POLYSACCHARIDES FOR ENHANCED OIL RECOVERY

C. G. Mothé[1*], *D. Z. Correia*[1], *F. P. de França*[2] *and A. T. Riga*[3]

[1]Department of Organic Processes/EQ/Federal University of Rio de Janeiro, CEP 21949-900, RJ, Brazil
[2]Department of Biochemical Engineering/EQ/Federal University of Rio de Janeiro, CEP 21949-900, RJ, Brazil
[3]Department of Chemistry, Cleveland State University, OH 44143, USA

Enhanced oil recovery process is based on the injection of chemical products (e.g. polymers, surfactants, gases) or thermal energy (originating from the injection of e.g. steam, hot water, in situ combustion) to recover crude oil. One of these processes use polymer solution to mobilize the oil in the reservoir. In this work the thermal decomposition kinetic of xanthan gum, guar gum and a blend (50/50 mass/mass%) was studied according to Ozawa–Flynn–Wall method. According to the kinetic analysis, the studied systems were copmpatible. The rheological behavior of the samples was studied in distilled water and seawater at different temperatures. Only the blend was studied in distilled water presented synergism (enhancement in material properties like stability and viscosity) which was confirmed through rheology.

Keywords: *enhanced oil recovery, polysaccharides and synergism*

Introduction

Enhanced oil recovery methods a long time ago have been employed in helping to prolong the life-time of oil and to obtain the maximum amount of recoverable oil. The efficiency of oil recovery during the primary stage is relatively low, leaving the majority of oil to be removed by secondary and/or tertiary recovery methods. The most common and the cheapest method of secondary oil recovery is waterflooding, where water is pumped into the reservoir forcing the oil to flow towards producing wells, however, inert gas injection or re-injection of produced gas can also be used [1, 2]. Regardless of the type of fluid used to displace the oil, it can bypass this oil and early breakthrough can occur. About 70% of the total petroleum still remains in the reservoir after application of primary and secondary techniques [3]. Tertiary or enhanced oil recovery (EOR) processes include all methods that use external sources of energy and/or materials to recover oil that cannot be produced economically by conventional methods. EOR processes can be classified as thermal methods (steam flooding, hot water drive, in situ combustion), chemical (polymer, surfactant) or miscible (hydrocarbon gas, CO_2, nitrogen) [4].

Some EOR techniques are suited to increase the recovery factor in light oil reservoirs, but a number, particularly those designed to reduce the in situ viscosity of the oil, are appropriate for heavy oil reservoirs. In situ combustion, for example, is a thermal method in which oil is ignited underground, creating a combustion front that is propagated through the reservoir by continuous air injection. In this process, a small portion of the oil in place is burned, producing heat that reduces the viscosity of the oil increasing its mobility. Large quantity of air is required because all the residual material remaining in the sand immediately in front of the combustion zone. Wet forward combustion is a recovery technique, which was conceived to improve the dry forward combustion in economical aspect. The air requirement is lower with water injection because less hydrocarbonous material is deposited on the sand grains and because all of the fuel is not necessarily consumed [5, 6].

Another method that involves mobility change is polymer flooding. In this case, water mobility is reduced due to an increase in its viscosity. Water-soluble polymers are employed in EOR as viscosifying agents of aqueous solutions used on oil recovery projects. The advantage of using polymers is that they are non-toxic and do not cause serious environmental problems [7]. The main role of the use of the polymers is to reduce the fluid displacement mobility. A secondary effect is a decrease in the relative water permeability in the reservoirs as a consequence of polymer adsorption. Since the last decades, petroleum industry has employed two types of polymers in the EOR projects: synthetics, mainly HPAM (partially hydrolyzed polyacrylamide) and polysaccharides like xanthan gum. These polymers have their rheological

---

[*] Author for correspondence: cheila@eq.ufrj.br

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

properties compromised by the conditions found in reservoirs like, high temperatures, high salinities, hardness of connate water, bacteria, etc. Therefore, the rheological study is essential for the choice and dimensioning of the types, volumes and concentration of the polymers used in EOR projects [8–10].

Xanthan gum is an extracellular polysaccharide produced by the bacterium *Xanthomonas campestris*. The gum consists of glucose backbone substituted by a charged trisaccharide side chain containing two mannoses and one glucuronic acid residues [11]. The secondary structure of xanthan can undergo a unique transition from a disordered random coil configuration where the side chains are oriented away from the backbone to a rigid, helical structure where the side chains are folded along the backbone. The transition depends on temperature and on ionic strength of the solution [12]. Xanthan is not readily shear degraded and is not susceptible to an increase in salinity or divalent ion concentration. Xanthan gum's disadvantages are the higher cost, high susceptibility to biodegradation and a potential for injection problems [13]. Guar gum is a galactomannan obtained from the endosperm of the *Cyamopsis tetragonolobus* seed. Because of its non-ionic nature, guar gum exhibits compatibility with salts over a wide range of electrolyte concentration. Xanthan side chains interact with guar gum. This interaction is favoured when the galactomannan has a high concentration of smooth regions, formed by mannose backbone without galactose radicals [14, 15].

Kinetic investigations are one of the most important applications of thermal analysis. Under the methods summarized by thermal analysis, differential scanning calorimetry (DSC) and thermogravimetry (TG) have outstanding significance. The common advantage of both these techniques, comparing to many other analytical methods is the ease way of sample preparation [16]. Kinetics can be used to study the interaction between materials. The kinetic parameters of the main degradation step of materials can be determined by the isoconversional method according to Ozawa–Flynn–Wall (O–F–W).

Ozawa–Flynn–Wall method is derived from the basic kinetic equation for heterogeneous chemical reactions and therefore having a wide application, since this is not necessary to know the reaction order or the conversional function $g(\alpha)$ to determine the kinetic parameters. The method is shown by the equation [17]

$$\log g(\alpha)=\log(AE_a/R)-\log\beta-2.315-0.4567E_a/RT \quad (1)$$

where $g(\alpha)$=conversion functional relationship, A=pre-exponential factor, E_a=apparent activation energy, R=general gas constant, β=heating rate, T=absolute temperature.

For different heating rates at constant degree of conversion α, Eq. (1) is:

$$\log\beta=-0.4567E_a/RT \quad (2)$$

The degree of conversion is defined as $\alpha=(m_0-m)/(m_0-m_f)$, where m_0, m, m_f refer to the initial, actual and final mass of the sample.

Apparent activation energy is calculated from the slope of the most probable straight line obtained by drawing the dependence $\log\beta$ *vs.* $1/T$ and the pre-exponential factor from the intercept of the straight line on the y axis. The activation energy determined is the sum value of activation energies of chemical reactions and physical processes in thermal degradation and therefore it is called apparent. The rate constant of the reaction is given by the Arrhenius equation.

$$k=A\exp(-E_a/RT) \quad (3)$$

In this work the non-isothermal degradation of xanthan gum, guar gum and a blend was investigated using thermogravimetric analysis. Kinetic parameters were calculated by Netzsch Thermokinetics 2 software to study a possible interaction. The behavior of these polysaccharides in solutions with different ionic strength was also evaluated by rheology. From thermal and rheological analysis, the synergism between xanthan and guar gums, which enhances the properties of materials like stability and viscosity was investigated.

Experimental

Samples

The two polysaccharides were used supplied by Plury Quimica Ltda. as courtesy, and produced by Rhodia. Guar gum HIGUM 55-I specifications are: molecular mass (*MW*) approximately 10^5; particle size is greater than 74 μm (traces) and lesser than 177 μm (90% minimun). The xanthan gum sample RHODIGEL 80 has a molecular mass around $2\cdot10^6$ and particle size between 75 μm (30% maximum) and 250 μm (90% minimum). Molecular mass and particle size data were supplied by Rhodia. The seawater used in rheological tests was from Saquarema's city (RJ/Brazil). Seawater was filtered to remove impurities and the total dissolved solids (TDS≈45 g L^{-1}) was determined setting 5 mL of sample in oven at 50°C until constant mass.

Methods

Thermal analysis

Thermogravimetric measurements were performed using TA Instruments SDT 2960 equipment. TG is a technique of thermal analysis that measures the mass loss either as a function of temperature or time in a varied and controlled atmosphere [18]. Experiments used around 10 mg of sample in their powdered form; xanthan/guar blend was made of 5 mg of each polysaccharide (50/50 mass/mass%). The temperature range varied from 30 to 800°C, and three heating rates were applied: 8, 10 and 12 K min^{-1}. Nitrogen was used as purging gas at a flow rate of 120 mL min^{-1}. Different heating rates were studied in order to obtain kinetic parameters, such as activation energy and pre-exponential factor. Inert atmosphere was used in order to study only the interaction of polysaccharides. If air was used as purge gas, oxidative reactions would confuse the results.

In order to determine the kinetic parameters of the main degradation step of xanthan, guar and the blend, the isoconversional method proposed by O–F–W was performed using the Netzsch Thermokinetics 2 software.

Rheological tests

Rheological tests were carried out using a Brookfield LV-DVIII rotational viscometer. The measuring geometry was a cone/plate sensor (CPE-50) and dynamic measurements were realized at shear rates between 50 to 450 s^{-1}. The measure of lower shear rates was not possible due to limitations of the cone/plate sensor. In the 20–65°C temperature range the effect of higher temperatures, simulating the temperature into the reservoirs was studied. The temperature control was performed using a TC501 Brookfield water bath. The samples analyzed were in 5000 ppm solutions. The polysaccharides were dispersed in distilled water or seawater at room temperature. The solutions remained at rest for 24 h, before the rheological measurements.

The study of solutions in seawater is justified by the use of polymers in offshore operations, since oil fields in the offshore environment, especially in the deepwater, represent a significant resource available to meet the expected increases in oil demand over the next decades [19]. Bagci *et al*. [20] studied the effect of brine composition on oil recovery by waterfloooding and found out that the highest recovery was obtained by the injection of 2% KCl+2% NaCl brine mixture. The oil recovery using this brine mixture was 18.8% higher than when distilled water was injected.

Results and discussion

Thermal analysis

Figures 1 to 3 exhibit the overlay of thermogravimetric curves at three different heating rates for guar gum, xanthan gum and the blend. Guar gum presented two decomposition stages and three decomposition stages were observed for xanthan gum and for the blend. The first mass loss is attributed to solvent evaporation derived from purification processes. The second stage, from 200 to 400°C, refers to the degradation of the polysaccharides. For xanthan gum and the blend, at 800°C around 20% of residue probably due to inorganic substances like calcium, sodium and potassium was obtained.

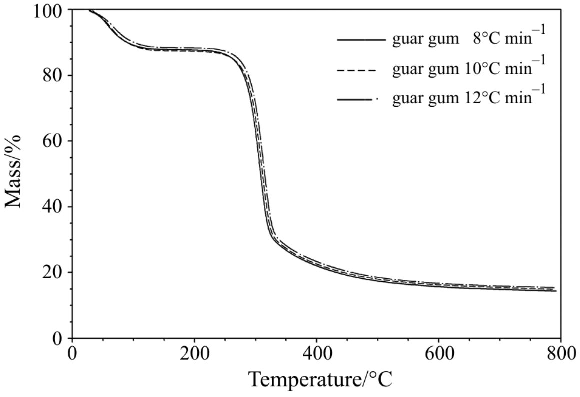

Fig. 1 TG curves of guar gum

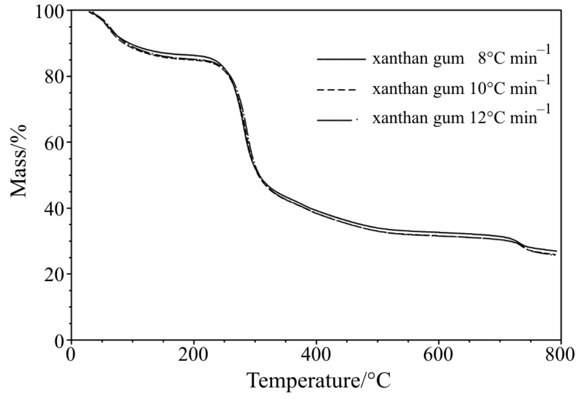

Fig. 2 TG curves of xanthan gum

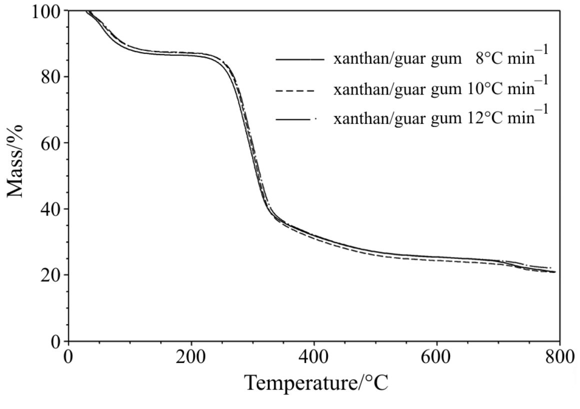

Fig. 3 TG curves of xanthan/guar blend

Table 1 Kinetic parameters of non-isothermal degradation of guar gum according to O–F–W model

α	E_a/kJ mol^{-1}	log$A$/s^{-1}	Sp*
0.020	172.42	13.54	12.73
0.050	171.68	13.54	12.87
0.100	168.69	12.98	13.00
0.200	172.57	13.33	12.95
0.300	175.06	13.58	12.89
0.400	178.27	13.89	12.83
0.500	180.96	14.14	12.80
0.600	184.41	14.46	12.75
0.700	189.55	14.93	12.70
0.800	205.84	16.36	12.58
0.900	629.86	52.69	11.95
0.950	1303.51	106.36	12.26
0.970	2034.67	163.26	12.46

The degradation of polysaccharides between 200–400°C was used for kinetic calculations. Applying the isoconversional analysis according to O–F–W method, to calculate the apparent activation energy (E_a) and pre-exponential factor (A) the conversions (α) varied between 0.02 and 0.97. The obtained values of (E_a) and (A) for guar, xanthan and the blend are shown in Tables 1 to 3.

On the basis of E_a value the estimated stability of the samples is not completely reliable, therefore some authors defend the application of compensation dependence when characterizing the thermal degradation process [17, 21]. A and E_a are related on the basis of an isokinetic relation:

$$\log A = a + b\log E_a \tag{4}$$

Instead of linear relationship for comparing the thermal stability of different systems, compensation parameter is used

$$Sp^* = E_a/\log A \tag{5}$$

The application of the compensation parameter eliminates the influence of experimental factors. In general, the greater the value of Sp*, the smaller is the reactivity of the system. The results (Tables 1 to 3) showed that guar gum and the blend exhibited greater Sp* compared to xanthan. It means that the degradation of xanthan requires less energy, therefore, xanthan is less stable. The value of the blend compensation parameter is between the ones in isolated polysaccharides, suggesting the compatibility of polysaccharides. It can be confirmed by the rheological behavior of all samples.

Table 2 Kinetic parameters of non-isothermal degradation of xanthan gum according to O–F–W model

α	E_a/kJ mol^{-1}	log$A$/s^{-1}	Sp*
0.020	210.00	18.32	11.46
0.050	189.33	16.00	11.83
0.100	192.67	16.21	11.89
0.200	189.62	15.78	12.02
0.300	188.64	15.63	12.07
0.400	193.53	16.06	12.05
0.500	200.77	16.72	12.01
0.600	215.79	18.08	11.94
0.700	257.04	21.75	11.82
0.800	388.83	33.20	11.71
0.900	1753.93	147.63	11.88
0.950	1639.16	132.07	12.41
0.970	973.03	76.68	12.69

Table 3 Kinetic parameters of non-isothermal degradation of xanthan/guar blend according to O–F–W model

α	E_a/kJ mol^{-1}	log$A$/s^{-1}	Sp*
0.020	164.99	13.35	12.36
0.050	171.51	13.93	12.31
0.100	178.08	14.51	12.27
0.200	185.14	15.11	12.25
0.300	196.36	16.11	12.19
0.400	209.16	17.23	12.14
0.500	218.40	17.97	12.15
0.600	224.01	18.36	12.20
0.700	228.68	18.64	12.27
0.800	243.70	19.81	12.30
0.900	486.94	40.31	12.08
0.950	1702.88	138.98	12.25
0.970	2314.75	185.38	12.49

Rheological tests

Figures 4 and 5 show the viscosity curves of guar gum in distilled water and in seawater, respectively. The viscosity measurements showed a pseudoplastic behavior, since the apparent viscosity decreases as shear rate increases. Guar gum was very sensitive to salt concentration and to temperature because the viscosity of its solutions presented a large decrease in seawater and in high temperature solutions. Viscosity curves of xanthan gum are exhibited in Figs 6 and 7. Xanthan gum had an increase in viscosity in seawater solutions. The negative charges of xanthan gum molecules are neutralized in the presence of salts and, especially at higher xanthan gum concentrations, the viscosity increases due to increased interaction between molecules [22]. Related the temperature, at 55 and 45°C, an increase in viscosity of xanthan solutions in distilled water was observed. It could be related to the gelation of xanthan at these temperatures. As it concerns to the blends (Figs 8 and 9), only the one prepared with distilled water exhibited synergism (increase in viscosity compared to the isolated polysaccharides). This happens due to the fact that xanthan polymer-polymer association is promoted by increasing salt concentration, owing to a reduction in intermolecular repulsion. The interaction between xanthan molecules is more favourable than xanthan/guar molecules in seawater [11]. In these synergistic blends, the viscosity values were higher at 55 and 65°C than at 35 and 45°C. Again, gelation of the blend should have been occurred in these temperatures. This behavior has been profitable in petroleum reservoirs, since temperatures underground are high. In this way, the use of the blend prepared with distilled water reduces the quantities of polysaccharide necessary to produce a specific viscosity.

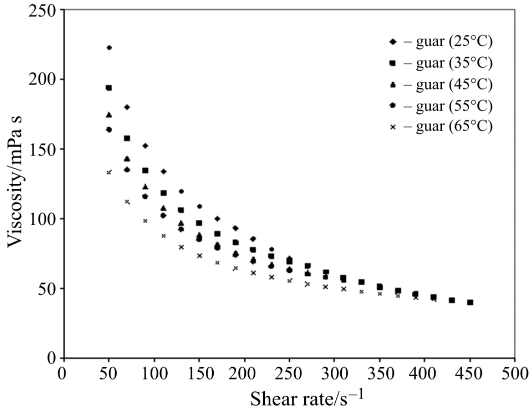

Fig. 4 Apparent viscosity *vs*. shear rate for guar gum in distilled water

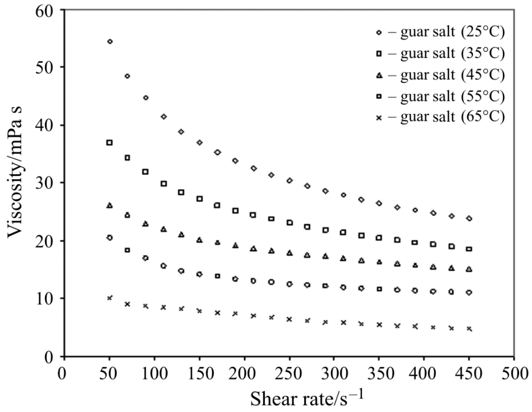

Fig. 5 Apparent viscosity *vs*. shear rate for guar gum in seawater

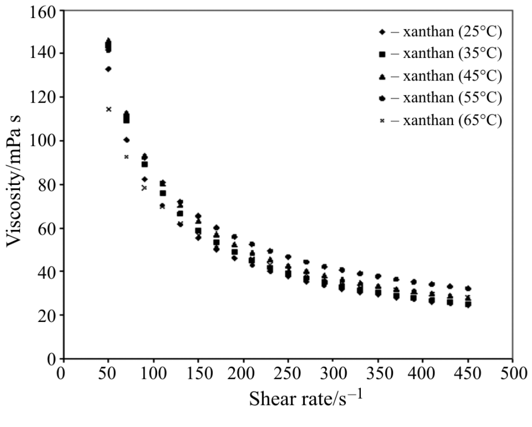

Fig. 6 Apparent viscosity *vs*. shear rate for xanthan gum in distilled water

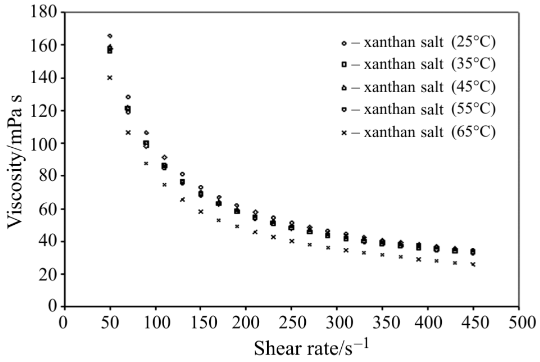

Fig. 7 Apparent viscosity *vs*. shear rate for xanthan gum in seawater

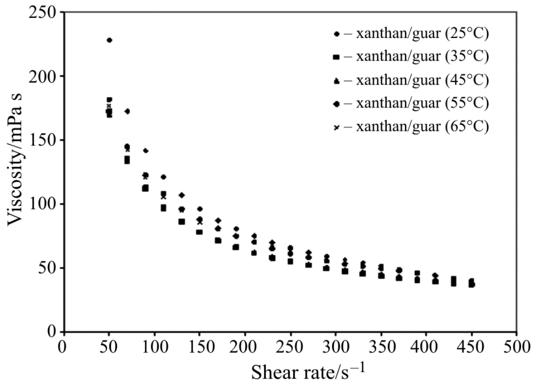

Fig. 8 Apparent viscosity *vs*. shear rate for xanthan/guar blend in distilled water

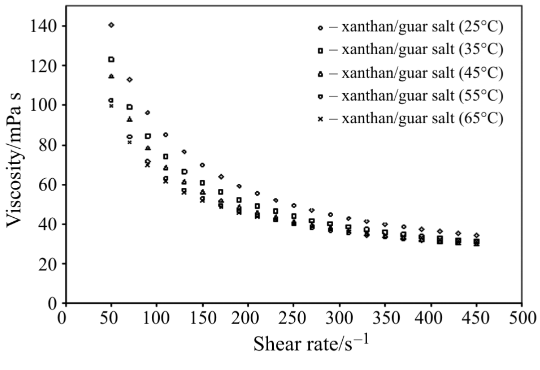

Fig. 9 Apparent viscosity *vs*. shear rate for xanthan/guar blend in seawater

Conclusions

Thermal decomposition kinetic study of xanthan gum and guar gum according to O–F–W method suggested an interaction between these polysaccharides since the blend formed by them presented compensation parameter value intermediary to the isolated gums. Rheological measurements showed that the synergism occurs only in low ionic strength solutions, and at 55 and 65°C an increase in viscosity values was observed. This behavior is interesting for polymer flooding operations into the reservoirs, temperatures are in this level or still higher and, this way, the costs with these polymers could be reduced. The use of seawater as solvent is an advantage in offshore operations, but it seems to be not suitable for blends formed by the gums used in our work.

Acknowledgements

The authors are grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support, to Plury Quimica Ltda. for supplying of the xanthan and guar gums, and to Netzsch do Brasil for providing the Thermokinetics 2 software.

References

1 T. Leslie, H. Xiao and M. Dong, J. Petr. Sci. Eng., 46 (2005) 225.
2 J. Moghadasi, H. Müller-Steinhagen, M. Jamialahmadi and A. Sharif, J. Petr. Sci. Eng., 43 (2004) 163.
3 S. Vossoughi, J. Petr. Sci. Eng., 26 (2000) 199.
4 B. Satter and G. C. Thakur, Integrated Petroleum Reservoir Management – A Team Approach, Penn Well Publishing Company, Oklahoma 1994, p. 175.
5 M. V. Kök, J. Therm. Anal. Cal., 56 (1999) 947.
6 S. Bagci and M. V. Kök, Fuel Process. Technol., 74 (2001) 65.
7 M. V. Kök and T. Alikaya, Petr. Sci. Technol., 21 (2003) 113.
8 R. A. Teixeira and P. S. M. V. Rocha, 3° Cong. Bras. P & D Petr. Gás, Bahia, Brazil, 2–5 October 2005.
9 C. P. Marcelino, A. C. M. Valentim, A. C. R. Medeiros, J. H. S. Girão and R. B. Garcia, Rio Oil & Gas 2004 Expo and Conference, Rio de Janeiro, Brazil, 4–7 October 2004.
10 D. Z. Correia, F. P. França and C. G. Mothé, Revista Conjuntura & Informação, 26 (2004) 9.
11 L. Lundin and A. M. Hermansson, Carbohydr. Polym., 26 (1995) 129.
12 V. P. Pai and S. A. Khan, Carbohydr. Polym., 49 (2002) 207.
13 K. C. Taylor and H. A. Nars-El-Din, J. Petr. Sci. Eng., 19 (1998) 265.
14 A. M. Goldstein, E. N. Alter and J. K. Seaman, Industrial Gums – Polysaccharides and their Derivatives, Academic Press, New York 1973, p. 303.
15 J. A. Casas, A. F. Mohedano and F. García-Ochoa, J. Sci. Food Agric., 80 (2000) 1722.
16 R. Opfermann, E. Kaisersberger and H. J. Flammersheim, Thermochim. Acta, 391 (2002) 119.
17 B. Andricic and T. Kovacic, Polym. Degrad. Stab., 65 (1999) 59.
18 M. V. Kök and C. Keskin, Thermochim. Acta, 369 (2001) 143.
19 P. L. Bondor, J. R. Hite and S. M. Avasthi, Latin. Amer. Carib. Petr. Eng. Conf., Rio de Janeiro, Brazil, 20–23 June 2005.
20 S. Bagci, M. V. Kök and U. Turksoy, Petr. Sci. Technol., 19 (2001) 359.
21 A. K. Galwey and M. E. Brown, Thermochim. Acta, 300 (1997) 107.
22 F. García-Ochoa, V. E. Santos, J. A. Casas and E. Gómez, Biotechnol. Adv., 18 (2000) 549.

DOI: 10.1007/s10973-005-7339-7