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THERMAL PROPERTIES OF JOJOBA WAX

II. OXIDATION BEHAVIOUR BY DIFFERENTIAL SCANNING CALORIMETRY

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The thermo-oxidative stability of Jojoba wax (Simmondsia chinensis) was studied by differential scanning calorimetry in a dynamic oxygen atmosphere. The thermo-oxidation activation energy (*Ea*) was calculated by determining the maximum reaction temperature (*Tm*) at different heating rates (*Hr*) and using mathematical models previously proposed for dynamic systems. The value obtained was 21.84 Kcal/mol. The oxidation enthalpies (ΔH_{ox}) were also calculated and a lineal relationship was found with the square root of the heating rate and the initial temperature of thermo-oxidation

Jojoba (Simmondsia chinensis) [1] is amongst the plants of the Sonoran Desert with the greatest possibilities as an important source of raw materials. Interest in this shrub is based on the fact that its seeds contain approximately 50% of a wax which is liquid at room temperature and made up of lineal esters of eicos-11-enoic, docos-13-enoic acids, and eicos-11-enol and docos-13-enol alcohols. These represent about 80% of the wax's composition determined by different techniques (gas chromatography, liquid chromatography, mass spectrometry) [2—4]. The double functionality of this wax (the ester function and the double bond) as well as its symmetry and linearity, give it an importance which, because of its lubricating properties [5], make it a potential substitute for sperm whale oil, as well as a raw material for the obtention of various derivative chemical products with such applications as lubricants, adhesives, factices, tenso-active agents, anti-foaming agents, etc. [1—6].

In spite of its importance, the thermal properties and polymorphous structure of Jojoba wax has received scant attention. There are some reports of DSC studies [7] which stand out, and another using X-rays in which the crystallization properties of the hydrogenated wax are studied [6]. The literature on the thermodynamic properties of this material is particularly scarce with the only reports being on fusion enthalpy [1], heat capacity [7], etc. The thermal and thermo-oxidative stability is one of the great potential advantages of Jojoba wax, as it is an effective lubricant at high pressures and temperatures. However, it is difficult to find reports which mention experiments done on this particular aspect, and to date there are accelerated evaluation which show its behaviour resistance to thermo-oxidative degradation.

Differential scanning calorimetry (DSC) has been used for several years to study the oxidation of polymeric material under accelerated conditions [8, 9] and its use has allowed the calculation of activation energies, oxidation enthalpies and other dynamic parameters, such as evaluation chemical stabilizers [10, 11] (antioxidants in natural and synthetic rubbers). Frequently, and because of its experimental simplicity, the dynamic method is used, which consists of subjecting the material to programmed heating in a dynamic oxygen atmosphere. In this way the material is brought into contact with an aggressive oxidizing medium in a gradually accelerated way, and the heat evolved in the process is determined simultaneously.

Some authors, amongst them Kissinger [12], Ozawa [13] and Barton [14], have developed a mathematical framework which allows the calculation of kinetic parameters, such as activation energy (Ea) from a series of experiments carried out in the manner already described. Equation 1 shows the mathematical relationship between the experimental parameters, heating rate, Hr; maximum reaction temperature, Tm; and the activation energy, Ea:

$$\ln Hr = C - Ea/RTm \tag{1}$$

where C is an arbitrary constant, Ea the activation energy in Kcal/mol, R the universal constant of the gases expressed in calories, Tm the maximum exotherm temperature and Hr the heating rate in K/min.

The determination of thermodynamic parameters is affected when the experiments are made at different masses and heating rates; displacements are found in the initial temperature due to thermal lag of the calorimetric cell (R). From the theory of flow calorimeters it has been deducted that the error ΔT is proportional to the square root of the heating rate of the melt heat or the dead mass. For this reason, to determine the real transition temperature with exactitude, it is important to carry out the determinations at different speed and extrapolate to $Hr = 0$. As well as being able to see a lineal relationship between $\sqrt[2]{Hr}$ and Tm the extrapolation will give the true transition temperature.

The studies done on waxes or triglycerides using DSC to determine their thermo-oxidative stability are few, however because of the simplicity of the method it is possible to apply this technique to the study of stability of unsaturated materials.

Experimental

Materials

The Jojoba wax used in these experiments was supplied by the Scientific and Technological Research Center of the University of Sonora (CICTUS). The liquid wax was mechanically extracted from the seed, the liquid filtered to eliminate insoluble impurities and used in this state. (As mentioned earlier, the composition of the wax has been studied and reported in previously weighed aluminium capsules with a microsyringe, weighed again and the weight of the wax calculated. The capsules were placed on the sample carrier.)

Thermal analysis

The instrument used in these studies was a Dupont 990 Thermal Analyzer coupled to a differential scanning calorimeter module. The calorimeter was calibrated periodically using synthetic sapphire for the ΔH quantitative determinations. The temperatures were corrected using indium, mercury, zinc and tin standards.

Different dynamic atmospheres, inert or oxydizing, were used during the experiments and gas flow (nitrogen or oxygen) was maintaned at 100 ml/min, previously dried by circulating over calcium chloride traps.

The thermo-oxidation enthalpies, ΔHox, were determined at different masses and heating rates. The masses varied between 1.1 – 2.5 mg and the heating rates, Hr, fluctuated between 2 – 20 K/min. Calculation of the thermo-oxidation enthalpy was carried out using the following equation:

$$\Delta H = 60\, ABE\, \Delta gs/m$$

where ΔH is the enthalpy used in mcal/mg, A is the total area in square inches, B is the recorder's speed in min/in., E is the calibration constant, Δgs is the sensitivity in mcal/seg-in., and m is the sample mass in mg.

The activation energies of the thermo-oxidation reactions were determined using samples with masses in the 2.0±0.5 mg range; heating rates, Hr, were varied between 2 – 50 K/min; and sensitivity oscillated between 0.2 – 4 mcal/seg-in. Because duplicating this type of reaction presents serious problems each step is an average of a minimum of five determinations. The oxygen or nitrogen atmosphere used was maintained at a constant flow of 100 ml/min, using a Nupro valve. Flow measurement was carried out using the soap bubble method, a technique commonly used in gas chromatography.

Results and discussion

The effect of the atmosphere on the stability of Jojoba wax is shown in Figure 1. All the determinations shown in this Figure correspond to a heating rate of 10°/min. A pronounced endotherm can be seen when pure nitrogen is used, starting at approximately 543 K with a maximum of 653 K. This endotherm corresponds to the evaporation of liquid wax and no original exothermic reaction is seen. When the nitrogen is contaminated with small traces of oxygen the evaporation endotherm diminished considerably and an exotherm which corresponds to oxidation reactions, appears. The initial and final heating capacities in both materials are not coincident because the nature of the components varies. The endotherm begins at the same temperature as the one previously described, however the maximum is 20 K less than that of pure nitrogen. Using oxygen the endotherm disappears leaving only the exotherm corresponding to the thermo-oxidation of the wax, which starts around 433 K and has a maximum temperature of 533 K. In the same way as the previous curves the heating capacity of the products and reagents before and after the reaction vary noticeably, indicating some alteration in the characteristics of the residual material with respect to the original. Table 1 shows some of the results obtained in oxidizing atmospheres at different heating rates, *Hr*. The results obtained for the thermo-oxidation enthalpy oscillate between 1434 to 1456 calories/g; depending on the heating rate, the temperature at which the oxidation reactions begin vary from 156.6° at a heating rate of 2°/min to 198.3° at a heating rate of 50°/min. Tracing the square root of the heating rate against the initial oxidation temperature a lineal relationship is seen which can be expressed by the following equation:

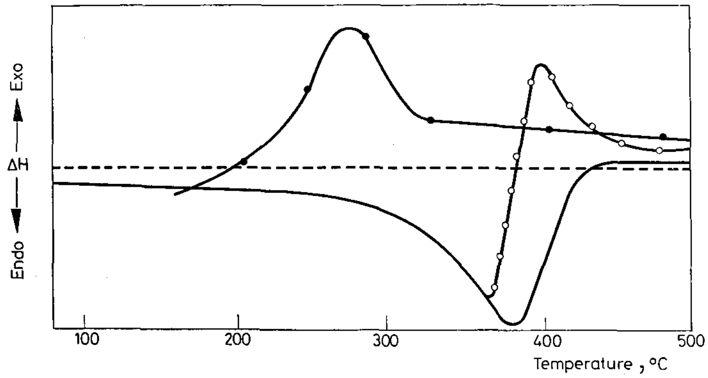

Fig. 1. Thermal behaviour of Jojoba wax in atmosphere of ——— high purity nitrogen, —○— commercial nitrogen, —●— oxygen. Heating rate 20 K/min

$$Hr^{1/2} = 0.1356\,T - 20.016.$$

The correlation index obtained was 0.98 and the temperature, *Ti*, for a heating rate equal to 0 is 147.6°.

Table 1

Utilized masses (mg) and sensitivities ((mcal/seg)/in) at each heating rate, as well as areas (in^2), enthalpies (mcal/seg) and initial temperatures of oxidation of Jojoba wax

Hr K/min	2	5	10	10	20	50
Mass, mg	1.3	1.1	1.3	2.5	1.4	—
Δgs, $\left(\frac{\text{mcal}}{\text{seg}}\right)$ in	0.2	0.2	1	1	2	—
Area, In^2	13.09	27.41	12.9	29.88	14.06	—
ΔH, mcal/mg	1456.01	1441.26	1434.8	1439.8	1452.19	—
Ti Ox, K	429.5	440.8	441.2	441.2	455.4	471.3

The studies of thermo-oxidative characteristics of Jojoba wax were continued to determine the activation energy corresponding to this process. As already mentioned, the experiments consisted of determining the maximum temperature of the thermo-oxidation exotherm at different heating rates and using the model proposed by Barton (Equation 1) to calculate the corresponding activation energy. Figure 2 shows the exotherms obtained at the different heating rates indicated and it can be seen that they are bimodal, becoming even more noticeable at higher heating rates. In Table 2 the corrected temperatures are shown for the two maxi-

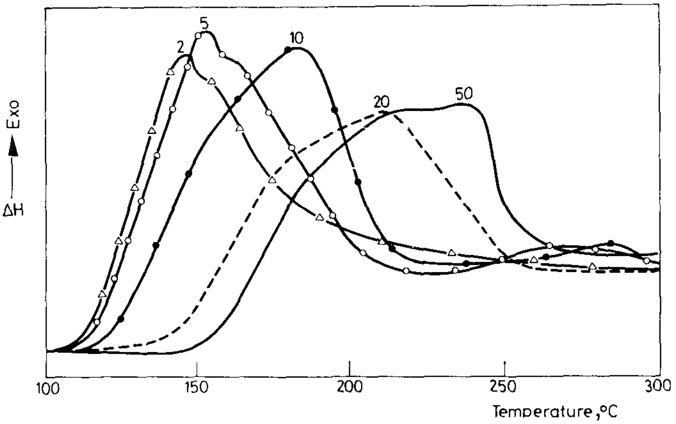

Fig. 2. Effect of the heating rate (K/min) (indicated in the maximum of each curve) on the shape and position of the exotherm of thermo-oxidation of Jojoba wax

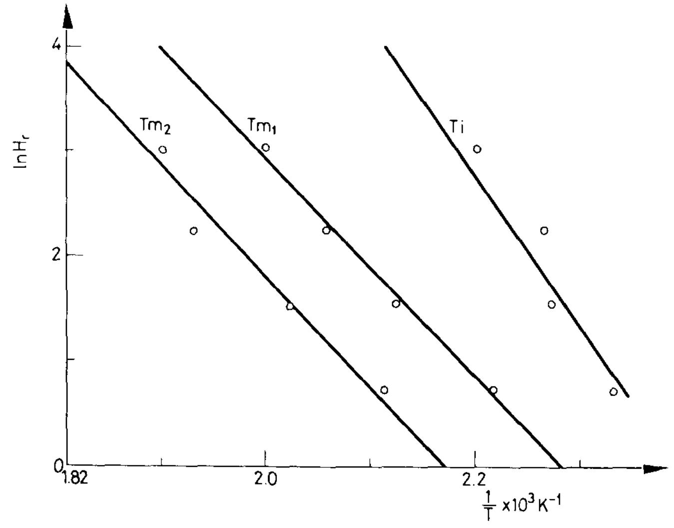

Fig. 3. Plots of ln Hr vs. $1/T$ for the two maximums of the exotherm in the thermo-oxidation of Jojoba wax

mums that appear in the thermal profile of the oxidation, as well as the corresponding heating rates. In separate columns the values corresponding to the inverse of each temperature seen, are also shown. With the results shown in Table 2, Figure 3 was drawn using the logarithm to trace the heating rate against the inverse maximum temperature of the corresponding exotherm. It can be seen that with both maximums a straight line is obtained from whose slope, using Equation 1, the corresponding activation energies were obtained and were 21.84 Kcal/mol in both cases.

Table 2

Temperature maximums (K) and inverses at each heating rates (deg/min)

Hr, K/min	Maximum 1		Maximum 2	
	Tm, °C	$1/T$ $K^{-1} \times 10^3$	*Tm*, °C	$1/T$ $K^{-1} \times 10^3$
2	176.7	2.222	199.2	2.117
5	196.3	2.130	220.5	2.025
10	210.6	2.067	243.8	1.934
20	221.8	2.020	249.6	1.912
50	246.4	1.924	275	1.824

Although to date no mechanisms have been proposed for the thermo-oxidation of Jojoba wax, it is possible to suppose that due to the insaturation of the carbon 11 it would be here where the degradation reactions start. Likewise the ester groups can present active places in this type of reaction. The contribution that DSC makes to the elucidation of the thermo-oxidation mechanisms of this type of material is reduced, limited to some kinetic and thermo-dynamic data which can be used in a complementary way for a better knowledge of this type of phenomena. For this reason works such as the present should be complemented with deeper studies on the reaction mechanism, using other techniques, such as gas chromatography for the elucidation of reaction products. However, the practical value of this type of experiment is indisputable as it can also be used as a tool for the elucidation of thermal or thermo-oxidative stabilities of materials which, like Jojoba wax, will be subject to drastic deterioration conditions. DSC could become a useful, rapid, quantitative tool for predicting behaviour through accelerated tests as presented in this paper.

Conclusions

Atmospheric influence on Jojoba wax degradation was studied by DSC and it was seen that when the oxidizing properties of the atmosphere rose the evaporation endotherm was gradually substituted for the thermo-oxidation exotherm. It was also found that the thermo-oxidation exotherm of Jojoba wax has bimodal characteristics which indicates that they are made up of two clearly distinguishable steps of thermo-oxidation. For each of these the maximum temperature at different heating rates was determined and from these results the corresponding activation energies were found to be 21.2 kcal/mol. Finally the lineal relationship between the square root of the heating rate and the initial thermo-oxidation reaction temperature could be seen.

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Résumé — On a étudié, par analyse calorimétrique différentielle dans une atmosphère dynamique d'oxygène, la résistance à l'oxidation thermique de la cire Jojoba (Simmondsia chinensis). On a calculé l'énergie d'activation (Ea) de l'oxydation thermique en déterminant la température maximale (Tm) de la réaction à diverses vitesses de chauffage (Hr) et en utilisant les modèles mathématiques déjà proposés pour des systèmes dynamiques. La valeur obtenue est 21.84 kcal/mole. On a calculé également les enthalpies d'oxydation (ΔH_{ox}) et on a trouvé des corrélations linéaires entre les racines carrées de la vitesse de chauffage et la température initiale de l'oxydation thermique.

Zusummenfassung — Die thermooxidative Stabilität von Jojoba-Wax (Simmondsia chinensis) wurde durch Differential-Abtastkalorimetrie in dynamischer Sauerstoffatmosphäre untersucht. Die Aktivierungsenergie der Thermooxidation (Ea) wurde durch die Bestimmung der maximalen Reaktionstemperatur (Tm) bei verschiedenen Aufheizgeschwindigkeiten (Hr) unter Anwendung der vorhergehend für dynamische Systeme vorgeschlagenen mathematischen Modelle berechnet. Der erhaltene Wert betrug 21.84 Kcal/Mol. Die Oxidationsenthalpien (ΔH_{ox}) wurden ebenfalls berechnet und lineare Zusammenhänge mit der Quadratwurzel der Aufheizgeschwindigkeit und der Anfangstemperatur der Thermooxidation wurden gefunden.

Резюме — Методом дифференциальной сканирующей калориметрии была изучена термоокислительная устойчивость Jojoba воска (Simmondsia chinensis) в динамической атмосфере кислорода. Энергия активации термо-окислительной реакции (E_a) была вычислена посредством определения максимума температуры реакции (T_m) при различных скоростях нагрева и используя математические модели, предложенные ранее для динамических систем. Полученное значение составляло 21.84 ккал/моль. Были также вычислены значения энтальпий окисления (ΔH_{ok}) и установлена их линейная зависимость между корнем квадратным скорости нагрева и начальной температурой термоокисления.