The Biodegradabilities of Different Oil-based Fatliquors

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Abstract

The biodegradabilities of different oil-based fatliquors derived from rape oil, fish oil, castor oil or mineral oil variants were investigated by evaluations of the respirations, BOD_5/COD values and COD, TOC removal ratios. Simultaneously, degradation kineticses of the fatliquors were also studied. The results indicate that the BOD_5/COD values and the COD, TOC removal ratios of all the natural oil based products are higher than 0.45 and 85%, respectively, which means all of them are biodegradable; while these values for the miner oil based fatliquors are lower than 0.2 and 10%, showing unbiodegradable characteristics; the biodegradability order is castor oil> fish oil> rape oil> mineral oil product. Further study indicates that the differences in biodegradability result from the fatty acid compositions (such as ricinoleic acid and polyunsaturated fatty acids) and active groups' content, higher contents of them are beneficial for modification reactions and biodegradation. The degradation kinetics studies reveal that the degradation rate constants (k) of castor oil, fish oil and rape oil product are 0.87, 0.84 and 0.81 d^{-1} for the sulfated fatliquor, and 0.95, 0.93, 0.85 d^{-1} for the oxidized-sulphited fatliquors, respectively; indicating that the degradation rates of oxidized-sulphited products are faster than the corresponding sulfated products; and no matter both for sulfated fatliqurs and oxidized-sulphited fatliqurs, the degradation rate for all samples shows an order of castor oil＞fish oil＞rape oil.

Key words: Biodegradability; Degradation rate, Different oil; Fatliquor

1. Introduction

Fatliquoring is one of the key operations in the leather manufacturing[1], it is an oil-addition process by which the leather fibers are lubricated so that after drying they will be capable of slipping over one another and producing an adequate compliance and softness.[2] Natural oil (such as rape oil, fish oil and castor oil) and mineral oil based fatliquors are the two kind of widely applied products in leather industry. Usually fatliquors need to be used in excess to ensure full penetration and complete reaction with leather fiber. As a result, a part of the fatliquors employed would inevitably remain in the float, leading to a high level of pollution emission. Moreover, it is the largest amount chemicals (10-20wt% on wet blue leather) used in the leather-making. So the biodegradability of fatliquors is one of the most important factors associated with environmental friendliness of leather industry.

Biodegradability of chemicals depends not only on the molecular structure of the tested compound but also on the microorganisms available, accessibility of metabolic cofactors (i.e. O_2, nutrients, etc.), growth medium and other environmental conditions, such as temperature and humidity.[3] However, the biomass, metabolic cofactors, growth medium and environmental conditions can be controlled with a standardized method. Therefore, the structure parameter, involving the main chain structure, substituted groups, polarity and active groups, is the key issue affecting the biodegradation. Knowing the relationship between the molecular structure and biodegradation of fatliquors could not only complement and substitute in part for some of the costly experimental evaluation of biodegradability but also help to identify and potentially avoid the production of new chemical compounds which are not easy to biodegrade. Thus, it would support the development of environmentally sustainable new products and the design of synthesis strategies that avoid poorly degradable intermediates and waste products.[4-5]

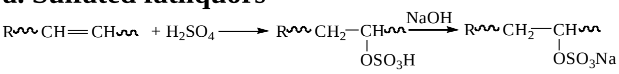
In our previous work, the rape oil was modified with different methods, such as sulfated, sulfonated, oxidized-sulphited, phosphated and copolymeric reactions, and the effects of different modification methods on the biodegradability of rape oil-based fatliquors were investigated. The results indicated the biodegradabilities of fatliquors were associated with different modification methods[6], and showed a biodegradability order of phosphated> sulfonated> oxidized-sulphited> sulfated> copolymeric; The modification method which consumed the hydroxyl groups and double bonds, such as sulfated modification would decrease the biodegradability, the others which did not consume those active groups, such as sulfonated and oxidized-sulphited, showed better biodegradability; for polymerization method, in one hand consumed the double bonds, on the other hand, possessed larger molecular size and steric effect, decreased the biodegradability[10]. As a continuous work, in this study, the different oils (rape oil, fish oil and castor oil) modified with the same method (sulfated or oxidized-sulphited), and the difference in their biodegradabilities and degradation kinetics were investigated in detail by using mineral oil-based fatliquors (alkyl sulfonyl chloride) as a reference; the purpose of this study is to investigate how the structure parameter of oils themselves influence the biodegradabilities of the modified products, finally to provide guidance for developing environmental-friendly fatliquors.

2. Experiments

Preparation of different oil-based fatliquors

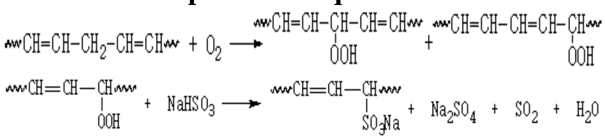
The fatliquors of different oil-based were prepared by sulfated reaction and oxidized-sulphited reaction according to the reference[7-8]. The reaction principles shown as follows:

a. Sulfated fatliquors



$$ROH + H_2SO_4 \longrightarrow R\text{-}OSO_3H \xrightarrow{NaOH} R\text{-}OSO_3Na$$

b. Oxidized-sulphited fatliquors



Characterizations

Iodine value and hydroxyl value were determined according to the ISO 3961 standard and AOCS standard methods Cd 13-60, respectively.[9] Fatty acid composition was determined by gas chromatography-mass spectrometry (GC-MS) (GC-MS TraceDSQII; ThermoFisher, USA) under the following conditions: oil transesterification to methyl esters; DB-5 capillary column 30 m × 0.25 mm i.d.; helium as carrier gas (40 kPa pressure); air pressure 100 kPa; hydrogen pressure 50 kPa; injection on column; flame-ionization detection at 220°C and ionization energy of 70 eV; programmed oven temperature from 80 to 260°C at 5°C/min.

Biodegradation is determined under aerobic conditions. Activated sludge from the aeration basin of a wastewater treatment plant treating predominantly domestic wastewater was used as the microbial biomass for the test. Before use the sludge was washed twice with tap water and starved under aeration for 24 h. The concentration of the activated sludge was determined[10] and expressed as mixed liquid suspended solids (MLSS). The pH of the activated sludge was adjusted to 6.8-7.2. In the test the fatliquors were added to a mineral medium (Ingredient[11]: KH_2PO_4 1 g/L, KNO_3 0.5 g/L, $MgSO_4 \cdot 7H_2O$ 0.1 g/L, $CaCl_2$ 0.1 g/L, $FeCl_3$ 0.01 g/L, NaCl 1 g/L) as the sole source of carbon, and the sealed vessels with a headspace of air were inoculated with activated sludge (suspended solids 4 g/L). The tests were run for 5 days at 20℃ with continuous shaking. Biodegradation is monitored by biological respiration curve, BOD_5/COD value, COD (chemical oxygen demand) and TOC (total organic carbon) removal ratios.

The COD and BOD (biochemical oxygen demand) were measured by using Hanna HI 99721 and HI 99724A-6 equipment, respectively (Hanna Instruments, Italy). The data are averages of three separate measurements. The COD removal ratio is defined as: COD removal ratio (%) = $(COD_0 - COD_5)/COD_0 \times 100$; Where COD_0 is the original COD of the test sample solution (mg/L), and COD_5 is the COD after the solution has been biodegraded for 5 days. TOC analyses were done using an Anatel TOC-2000 TOC analyzer (Shimadzu, Japan). The TOC removal ratio is defined as: TOC removal ratio (%) = $(TOC_0 - TOC_5)/TOC_0 \times 100$; Where TOC_0 is the original TOC of the test sample solution (mg/L), and TOC_5 is the TOC after the solution has been biodegraded for 5 days.

3. Results and Discussion

Analysis of fatty acids compositions of the oils

Rape oil, castor oil and fish oil are three of the most typical natural renewable oils, and mineral oil is a representative of nonrenewable fossil oil. These oils have a wide range of applications in the leather industry as fatliquors. Rape oil, castor oil or fish oil based sulfated or oxidized-sulphited fatliquors, as well as the alkyl sulfonyl chloride fatliquors are frequently-used natural or mineral oil based fatliquors, respectively. Their fatty acid compositions (summarized in Table 1) differ from each other. Table 2 lists their statistic saturated, monounsaturated and polyunsaturated fatty acids contents. As can be seen from Table 1 and Table 2, in castor oil there are huge amounts of ricinoleic acid (Figure 1), which contains hydroxyl group on the backbone of the molecular, and the lowest amount of saturated fatty acids. However, no hydroxyl group containing fatty acid is involved in other oils. The polyunsaturated fatty acids (in the form of EPA, DHA and heneicosapentaenoic acid, see Figure 1) contents reach 1/3 in fish oil, while the monounsaturated fatty acids in rape oil are the majority and polyunsaturated fatty acids existed only in the form of biunsaturated or triunsaturated fatty acids. For the mineral oil, the saturated hydrocarbons are the major component and no hydroxyl groups and little double bonds can be found in the mineral oil.

Table 2 The statistic saturated, monounsaturated and polyunsaturated compositions contents for different oils (%)

Oil	Saturated	Monounsaturated	Polyunsaturated
Rape oil	24.7	59.3	18.0
Fish oil	27.8	39.2	33.0
Castor oil	12.6	79.9	7.5
Mineral oil	98.4	1.6	-

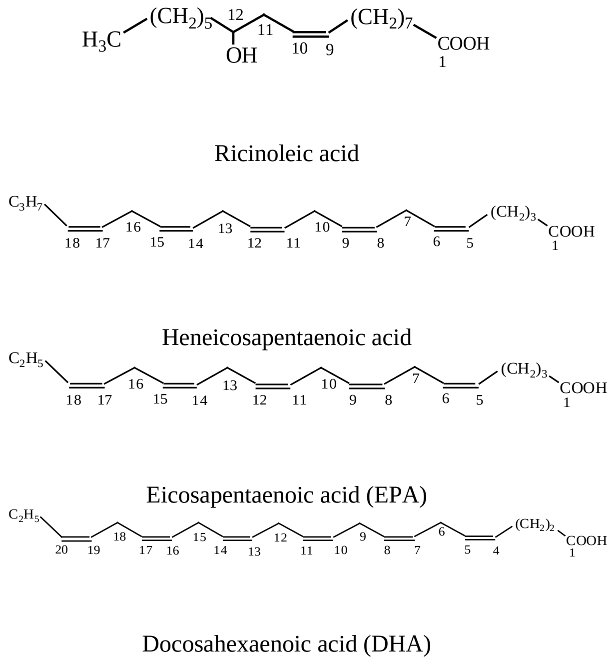


Figure 1 Molecular structure of ricinoleic acid and polyunsaturated fatty acids

Table 1 The fatty acid composition of the oils

	Fatty acid	Molecular formula (number of double bonds)	Composition (wt.%)
Rape oil	Palmitoleic acid	$C_{16}H_{30}O_2$ (1)	0.7
	Palmitic acid	$C_{16}H_{32}O_2$ (0)	16.2
	Heptadecaenoic acid	$C_{17}H_{32}O_2$ (1)	0.9
	Linolenic acid	$C_{18}H_{30}O_2$ (3)	2.7
	Linoleic acid	$C_{18}H_{32}O_2$ (2)	15.2
	Oleic acid	$C_{18}H_{34}O_2$ (1)	54.2
	Stearic acid	$C_{18}H_{36}O_2$ (0)	6.3
	Gadoleic acid	$C_{20}H_{38}O_2$ (1)	2.6
	Arachidic acid	$C_{20}H_{40}O_2$ (0)	1.2
Fish oil	Myristic acid	$C_{14}H_{28}O_2$ (0)	5.6
	Palmitoleic acid	$C_{16}H_{30}O_2$ (1)	7.8
	Palmitic acid	$C_{16}H_{32}O_2$ (0)	15.4
	Margaric acid	$C_{17}H_{34}O_2$ (0)	3.2
	Stearic acid	$C_{18}H_{36}O_2$ (0)	4.6
	Oleic acid	$C_{18}H_{34}O_2$ (1)	13.9
	Gadoleic acid	$C_{20}H_{38}O_2$ (1)	7.1
	Eicosapentaenoic acid (EPA)	$C_{20}H_{30}O_2$ (5)	14.7
	Heneicosapentaenoic acid	$C_{21}H_{32}O_2$ (5)	5.4
	Erucic acid	$C_{22}H_{42}O_2$ (1)	9.4
	Docosahexaenoic acid (DHA)	$C_{22}H_{32}O_2$ (6)	12.9
Castor oil	Palmitic acid	$C_{16}H_{32}O_2$ (0)	2.3
	Margaric acid	$C_{17}H_{34}O_2$ (0)	8.1
	Stearic acid	$C_{18}H_{36}O_2$ (0)	2.2
	Oleic acid	$C_{18}H_{34}O_2$ (1)	0.7
	Linoleic acid	$C_{18}H_{32}O_2$ (2)	7.5
	Ricinoleic acid	$C_{18}H_{34}O_3$ (1)	79.2
Mineral oil	Saturated hydrocarbons	C_nH_{2n+2} (n=11-24)	98.4

The biodegradabilities of different oil-based sulfated fatliquors

As it is known, the activated sludge process is an efficient and widely used method in wastewater treatment[12]. Respiration is the essential activity of aerobic microorganisms in the activated sludge. The respiration of activated sludge will be different from its endogenous respiration when there are chemicals in wastewater. Thus, the biodegradability of the fatliquors can be qualitatively evaluated by comparing the difference in biological respiration curves[13]. When a biodegradable chemical is utilized as the source of carbon and the energy for the growth of the organisms in activated sludge,

the respiration of activated sludge will be enhanced. The respiration curves of rape oil, fish oil, castor oil based sulfated fatliquors and mineral oil-based fatliquors (alkyl sulfonyl chloride) as well as the endogenous respiration curve are shown in Figure 2. The respiration curves of the three natural oil-based fatliquors are all above the endogenous respiration curve, which means all of them are biodegradable. And the respiration curve of activated sludge in presence of castor oil based fatliquors is

higher than others, while the rape oil one is the lowest of the three natural oil based fatliquors, indicating that the biodegradability of the castor oil type fatliquors is the best, and the biodegradability of rape oil based fatliquors is not as good as other two. However, the respiration curve of the alkyl sulfonyl chloride is lower than endogenous respiration curve, suggesting that the mineral oil based fatliquors could not be biodegraded by the activated sludge.

The biodegradability of a chemical can also be evaluated by the value of BOD_5/COD, which is a simple method to evaluate the biodegradability of organic compounds. A higher BOD_5/COD ratio is associated with a better biodegradability. A compound is usually considered as an easily biodegradable one when its BOD_5/COD value is higher than 0.45. On the contrary, it is considered as a hardly biodegradable one when the value is lower than 0.20. As shown in Table 3, the BOD_5/COD value is greater for castor oil based fatliquors than for other fatliquors and the values of the natural oil fatliquors are all higher than 0.45 and alkyl sulfonyl chloride's is lower than 0.2, indicating all natural oil-based fatliquors are biodegradable, while the mineral oil fatliquors is not biodegradable, and the biodegradability shows an order of castor oil fatliquors > Fish oil fatliquors > Rape oil fatliquors > alkyl sulfonyl chloride.

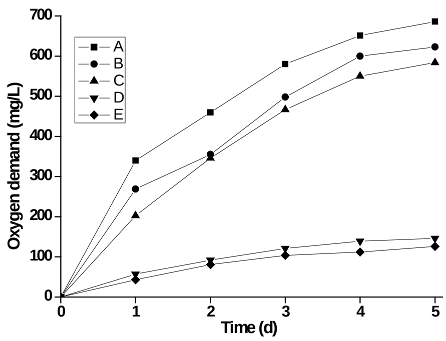


Figure 2 The respiration curves of different oil-based sulfated fatliquors (A: castor oil; B: fish oil; C: rape oil; D: the respiration curves of activated sludge; E: mineral oil)

Table 3 BOD_5/COD values and COD, TOC removal ratios of different oil-based sulfated or oxidized-sulphited fatliquors in 5 days of biodegradation

Fatliquors		BOD_5/COD	COD_0 (mg/L)	COD_5 (mg/L)	COD removal (%)	TOC_0 (mg/L)	TOC_5 (mg/L)	TOC removal (%)
alkyl sulfonyl chloride		--	558	530	4.98	553	525	5.02
castor oil	sulfated	0.97	557	5	99.1	661	5	99.2
	oxidized-sulphited	0.98	561	4	99.3	674	3	99.5
Fish oil	sulfated	0.92	519	12	97.7	541	9	98.3
	oxidized-sulphited	0.95	525	10	98.1	559	6	98.9
Rape oil	sulfated	0.87	500	50	90.0	527	36	93.2
	oxidized-sulphited	0.93	510	33	93.5	543	26	95.2

-- BOD_5 undetectable

The oxygen consumption is characterized by COD value and it is commonly used as a crucial parameter to reflect total content of pollutions in the wastewater. Therefore, the degree of COD removal ratio of a chemical after treating with activated sludge for 5 days is able to characterize the efficiency of biological treatment process and the biodegradability of the fatliquors. However, due to the physical adsorption of the activated sludge to the chemicals, the COD value cannot solely reflect the biodegradation. Thus, the biodegradation should be further confirmed by the TOC removal ratio analysis. When the soluble carbon of the biodegradable chemicals in the wastewater is utilized as the source of carbon and energy for the growth of organisms in activated sludge,[14] it will be gradually consumed by the organisms, resulting in the decrease of the TOC value. So the biodegradability of a chemical can also be characterized by the degree of TOC removal after treating with activated sludge. Similarly, the COD removal ratio order of these fatliquors is castor oil> Fish oil> Rape oil> alkyl sulfonyl chloride, and the COD removal ratios are all higher than 85% for the natural oil fatliquors and lower than 10% for mineral oil fatliquors, showing as the same tendency as the respiration curves result. This conclusion can be further confirmed by the TOC removal ratio analysis. As can be seen from Table 3, the TOC removal ratios of all the natural oil fatliquors are higher than 85%, and mineral oil fatliquors is lower than 10%, which in agree with the order of the COD removal ratios.

The difference in the biodegradabilities of these fatliquors should be attributed to different fatty acid compositions and active groups' content in fatliquors after modification. As mentioned in figure 1, the sulfated reaction mainly consumed double bonds and hydroxyl groups, so after modification the hydroxyl and iodine values were decreased for all samples as shown in Table 4. For castor oil the hydroxyl value is still higher than the others whilst the iodine value is almost as the same as other products after modification. It is believed that due to their electron supplying effect the hydroxyl groups have played an important role in biodegradation. For fish oil and rape oil based fatliquors, it is another case. It is the double bond content dominantly influences their biodegradation rather than the hydroxyl groups' content. Comparing with the fish oil and rape oil, the iodine value in the former is higher than in the latter, but after modification the iodine values are almost the same. This should be attributed to the polyunsaturated fatty acids (such as EPA, DHA and heneicosapentaenoic acid , see figure 3) content in the oils, the former is greater for the latter, and these non-conjugated double bonds are beneficial for both modification reactions and biodegradation. In rape oil, the double bonds existed mainly in the monounsaturated fatty acids, and the activity of these double bonds is less than the non-conjugated double bonds, hence the biodegradation by cleavage the double bond is slower than the polyunsaturated fatty acids; that is why the biodegradability of rape based fatliquors is inferior to the other two products. However, the saturated hydrocarbon derivatives are the major components and no hydroxyl groups or double bonds are involved in the mineral oil fatliquors. It is believed that the long chain alkyl groups (long C-C chains) are quite difficult to be cleaved by biodegradation, and the existence of the strong electron-withdrawing group (-Cl) further decrease its biodegradability.

Table 4 The iodine and hydroxyl values of the fatliquors before and after modification

	Oil	Castor oil	Fish oil	Rape oil
Iodine value (gI/100g)	before modification	85	176	106
	sulfate modification	41	49	42
	oxidized-sulfite modification	72	152	84
Hydroxyl value (mgKOH/g)	before modification	170	10	11
	sulfate modification	55	5	7
	oxidized-sulfite modification	165	8	9

The biodegradabilities of oxidized-sulphited fatliquors

Fig. 3 displays the respiration curves of the oxidized-sulphited fatliquors and mineral oil based fatliqors, as well as the endogenous respiration curve of the activated sludge. It can be seen that the substrate respiratory curves of the natural oil fatliquors are all above the endogenous respiration curve, showing good biodegradabilities. On the contrary, the respiratory curves in presence of alkyl sulfonyl chloride is below the endogenous respiration curve which means the alkyl sulfonyl chloride can hardly be degraded by the microorganism. Similar conclusions can be draw from the analysis of BOD_5/COD values, COD and TOC removal ratios. As shown in table 3, the natural oil based oxidized-sulphited fatliquors are easy to be degraded whilst the mineral oil based fatliquors is hardly degraded.

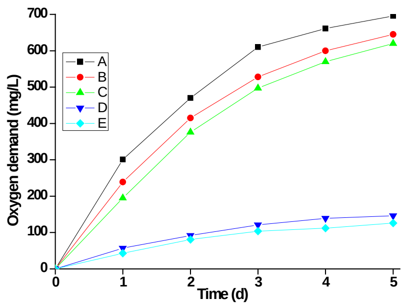


Figure 3 The respiration curves of different oil-based oxidized-sulphited fatliquors (A: castor oil; B: fish oil; C: rape oil; E: mineral oil; D is the respiration curves of activated sludge).

For oxidized-sulphited reaction, the reaction position is the allylic hydrogens (α-CH2) of unsaturated fatty acids. Theoretically, the double bounds and hydroxyl groups are not consumed, but actually partial double bonds are consumed for the partial oxidative degradation decomposition of unsaturated fatty acids into small compounds with –CHO or –COOH.15 So after modification the hydroxyl values and iodine value are just decreased a little for all samples as shown in Table 4, this little decrease does not change the order of hydroxyl value iodine value for all samples, so the biodegradability of oxidized-sulphited fatliqurs show the same order as the sulfated fatliquors.

The biodegradation kinetics of different oil based fatliquors

The respirations, BOD_5/COD values and COD, TOC removal ratios analysis can provide a possibility of biodegradation but cannot tell which one biodegrade faster or slower. Previous studies indicated that the BOD with time of low concentration organic compound under activated sludge treatment, approached to single-molecule reaction mechanism, and accorded with first-order reaction kinetics model[16]. Assume that the ultimate BOD is L_0, and then at time t the respiration rate is proportional to the residual BOD Lt, and can be derived as equations (1) and (2):

$$\frac{dL_t}{dt} = -kL_t \qquad (1)$$

Thus, $$y_t = L_0 - L_0 \exp[-k(t - t_0)] \qquad (2)$$

Where, L_0 represents the ultimate BOD (mg/L), and Lt is the total remaining BOD at time t (mg/L); t is the biodegradation time (d); y_t is the BOD at time t (mg/L); k is the rate constant of BOD (1/d); t_0 is persists time (d).

This model contains three kinetics parameters, which reflects the different biodegradabities of these fatliquors. L_0/COD is the direct reflection of the degree of degradation; k describes degradation rate and t_0 reflects the adaptability of the activated sludge with fatliquors. Based on the model, table 5 gives the values for the model parameters after model optimization. The degradation rate constants (k) for all the oxidized-sulphited samples are larger than the corresponding sulfated samples, revealing that the biodegradation rates of sulfated fatliquors are inferior to the oxidized-sulphited fatliquors. No matter both for sulfated products or oxidized-sulphited products, the k values all show a order of castor oil fatliquor> fish oil fatliquors> rape oil fatliquors, which means the degradation rate of fatliquors also shows the order of castor oil> fish oil> rape oil. Biodegradation kinetics study also confirms the above conclusion, that is, the biodegradability of different oil-based fatliquors are mostly associated with the fatty acid compositions and actives groups (double bonds and hydroxyl groups) content in the oils, higher contents of them are beneficial for their biodegradation.

Table 5 Model parameter values for the fatliquors

		COD (mg/L)	t_0 (h)	k (1/d)	L_0 (mg/L)	Biodegradation (%)
Castor oil	sulfated	557	1.54	0.87	549	98.5
	oxidized-sulphited	561	1.04	0.95	557	99.3
Fish oil	sulfated	519	2.14	0.84	486	93.7
	oxidized-sulphited	525	1.35	0.93	507	96.5
Rape oil	sulfated	500	2.43	0.81	446	89.2
	oxidized-sulphited	510	2.39	0.85	479	93.9

4. Conclusions

(1) The fatty acid composition is the most important issue associated with the biodegradabilities of different oil-based fatliquors; the hydroxyl group containing fatty acid (ricinoleic acid) and non-conjugated polyunsaturated fatty acids, such as EPA, DHA and heneicosapentaenoic acid are beneficial for both modification reactions and biodegradation.

(2) The content of the actives groups (double bonds and hydroxyl groups) depend on the fatty acid composition and further affect the biodegradabilities of these fatliquors. A high content of unsaturated fatty acids and hydroxyl groups increases the biodegradability of fatliquors.

(3) The biodegradability of natural oil based fatliquors is superior to mineral type, and reveals the order of castor oil>fish oil>rape oil>mineral oil.

(4) The degradation kinetics studies show the degradation rates of oxidized-sulphited oils are faster than the corresponding sulfated oils; the fish oil fatliquors degrades slower than castor oil fatliquors but faster than the rape oil fatliquors, for both sulfated and oxidized-sulphited modification.

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