Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Continuous Extraction of Crude Tall Oil

J. M. F. Nogueira[a]
[a] CHEMISTRY DEPARTMENT, UNIVERSITY OF LISBON, LISBON, PORTUGAL

To cite this Article Nogueira, J. M. F.(1997) 'Continuous Extraction of Crude Tall Oil', Separation Science and Technology, 32: 17, 2807 — 2820
To link to this Article: DOI: 10.1080/01496399708002223
URL: http://dx.doi.org/10.1080/01496399708002223

SEPARATION SCIENCE AND TECHNOLOGY, **32**(17), pp. 2807–2820, 1997

Continuous Extraction of Crude Tall Oil

J. M. F. NOGUEIRA
CHEMISTRY DEPARTMENT
UNIVERSITY OF LISBON
CAMPO GRANDE ED. C1, 1700 LISBON, PORTUGAL

ABSTRACT

A new continuous extraction method for fatty and resinic acids separation from crude tall-oil sodium salts aqueous solutions by countercurrent contact with *n*-heptane was developed using a bench-scale multistage mixer-settler plant. The data obtained showed good recoveries and high purities, especially for resinic fraction stream, for which the consumption of chemical reagents is virtually obviated with consequent economic advantages.

Key Words. Crude tall oil; Fatty acids; Resinic acids; Dissociation extraction; Continuous extraction; Mixer-settler extractors

INTRODUCTION

Crude tall oil (CTO) is a raw material rich in long-chain fatty and diterpenic or resinic acids (1). It has important applications in several industries (2).

The fractionation of CTO in plants is by distillation under high vacuum, which yields fractions of fatty and resinic acids with substantial purity (3). However, such separations are frequently uneconomic because they usually involve high operating costs, especially great energy consumption. Also, this way of treating such high molecular weight, low price materials leads to considerable pitch formation due the heat-sensitive constituents, and promotes isomerization, disproportionation, and pyrolysis reactions (4).

Actually, with CTO production below 100,000 ton/year as the main byproduct of cellulose production from pine wood, a distillation plant investment is not justified. In some cases the producers can only burn or sell CTO for a price related to its heat capacity (5).

Solvent extraction as an alternative to distillation shows growing implementation in the process industry, caused by remarkable development in a wide range of technological applications, especially in hydrometallurgy and environmental impact (6).

Although studies of liquid–liquid extraction of CTO have been carried out since the 1940s with no conclusive results, separation studies of fatty and resinic acids by the solvent extraction technique represent an alternative unit operation to traditional distillation practice in the industry if enough selectivity and economic advantages can be obtained.

As was previously reported in systematic *batch* studies (7), the application of dissociation extraction methodology for CTO fractionation, when using controlled conditions of pH, CTO concentration, solvent affinity, ionic strength, amphiphilic behavior and in the absent of organic extractants, demonstrated very interesting results. Such data were well supported by a theoretical mathematics approach based on the differential solubility found among fatty and resinic acidic fractions due the competition between organic and aqueous phases. However, those studies would be better understood by industry if continuous extraction of cheap CTO could be implemented, together with enough selectivity and high recovery, without significant chemical and energy consumption.

For such a purpose, the theoretical stage calculation needed to achieve a particular separation when using a multistage extraction must be done based on previous data obtained from systematic *batch* studies in order to better optimize the overall continuous process. This could be made either by a stage-to-stage procedure, which is accurate but laborious, or by a graphical approach similar to McCabe–Thiele methodology for distillation. The latter is extensively used in commercial processes, especially in the presence of complex systems (8). Details for graphical methodology can be understood by using the isothermal distribution data, which always involve additional simplification assumptions, but a reasonable accuracy is usually obtained (9).

For CTO systems in particular, continuous extraction of long-chain fatty and resinic acids by a multistage process would involve adequate extraction, washing, and stripping sections. When a low stage number is required ($N \leq 6$), as well as minimum residence time due the high mass transfer rate, mixer-settler extractors are used to promote good performance and easy operation to obtain high yields (10, 11).

The present paper reports a fresh approach to fatty and resinic acids separation from Portuguese CTO by dissociation extraction using a bench-scale countercurrent multistage continuous plant (12).

EXPERIMENTAL

Reagents and Solvents

All solvents and reagents used were commercial products of more than 99% purity (GC). A CTO sample from Portuguese Pulp and Paper Industry (Portucel SA, Rodão) with the characteristics shown in Table 1 was used, according to ASTM D 803 (13).

Dibutylphthalate [Merck: Art. 800919—better than 99.5% purity (GC)] was used as an internal standard in chloroform (2 mg/mL) for GC analysis.

Diazomethane was obtained from *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide dissolved in diethyl ether (5%) by reaction with potassium hydroxide in ethanolic aqueous solution. By using bubbling nitrogen gas, fresh diazomethane was obtained. It esterified the carboxylic acids samples as recommended in ASTM D 3008 (14).

Methodology

Distribution data of the equilibrium extraction isotherms for fatty and resinic acids were obtained by contacting an aqueous solution containing CTO sodium salts ([CTO] = 1.011 g/L, pH 9.2, T = 30°C) with *n*-heptane in separatory flasks (125 mL) and using the phase ratio variation method (15) ranging from 10/100 to 100/10 (mL). Both phases were shaken for 20 minutes and left standing for 2 hours in a thermostat at 30°C before samples of each phase were taken and quantified.

Distribution data of the equilibrium scrubbing isotherms for fatty and resinic acids were made by contacting *n*-heptane, which contained both

TABLE 1
Characteristics of the Portuguese CTO Sample

Acid number	156.6
Saponification number	179.4
Unsaponifiable matter	13.1%
Water content	1.5%
Fatty acids	37.5%
Resinic acids	49.4%

acids previously obtained from one stage of extraction, with a dilute aqueous solution of sodium hydroxide ($T = 30°C$, pH 10.5), using a procedure similar to that employed above. All distribution data were the average of two experiments.

For continuous tests the feed solution was an accurately weighed sample of CTO suspended in water with a 1% excess of sodium hydroxide and diluted to the desired concentration ([CTO] = 3.5 g/L). The correct pH (Orion model 420 A) was attained through small additions of an aqueous solution of hydrochloric acid. The feed solution was stored in a plastic tank and homogenated with a mechanical stirrer (Ika Werb model RE 162). The organic solvent used was *n*-heptane. Aqueous solutions of sodium hydroxide (concentrations of 0.1 and 1 g/L) were used for scrubbing and stripping circuits respectively. All liquid circuits were connected by means of neoprene and viton tubes (3.2 mm i.d.).

A bench-scale countercurrent multistage plant, which worked continuously for 18 hours at room temperature after steady-state of controlled conditions had been established, consisted of a battery of mixer-settlers built of PVC-glass with rectangular settlers (1200 mL) and square mixers (520 mL). Turbine impellers connected to a pump-mix type (Ika Werb model RE 16) and working at 1000 rpm (Kane-May 6001) were adopted. Peristaltic pumps (Watson Marlow model 503 U/RL) were used for CTO feed solution (15 mL/min), *n*-heptane (105 mL/min), scrubbing solution (30 mL/min), stripping solution (18 mL/min), and storage plastic tanks for inlet and outlet liquid phases.

Analytical Procedure

Organic phases (2 mL) were evaporated under nitrogen, diluted in diethyl ether/methanol (9:1), and esterified with freshly prepared gaseous diazomethane. Aqueous phases (5 mL) were acidified with hydrochloric acid ($pH < 1$), extracted with 5 mL of diethyl ether/methanol (9:1), and finally (2 mL) also esterified with diazomethane.

Dibutylphthalate solution was added (1 mL) as an internal standard to the methylated samples after nitrogen evaporation.

A Hewlett-Packard 5890 A gas chromatograph, equipped with a flame ionization detector [FID: air/hydrogen (high grade)] and a capillary inlet system with a glass liner tube (HP part no. 18740-60840), using the parameters shown in Table 2, was used for quantification (16). The data were reported in a HP-3396 electronic integrator, and calibration plots were made. Oleic and linoleic acids were quantified in the fatty fraction; abietic, dehydroabietic, isopimaric, palustric, primaric, neoabietic, and sandaracopimaric acids were quantified in the resinic fraction.

TABLE 2
Conditions and Parameters Used in GC Analytical Method (16)

Column	Fused silica capillary (HP-5); 25 m; 0.20 mm i.d.; 0.33 μm of film thickness: 5% biphenyl, 95% dimethyl polysiloxane liquid phase (crosslinked)
Injection	1 μL (Hamilton 710 N syringe); "hot needle technique"
Carrier gas	Nitrogen (high grade); linear flow 20 cm/s
Split ratio	1:100
Injector temperature	260°C
Detector temperature	260°C
Oven temperature	220°C isothermal

All analyses were done in triplicate.

RESULTS AND DISCUSSION

Distribution Data

Previous *batch* studies (7) of the main factors affecting this system showed the effectiveness of dissociation extraction for CTO separation into fatty and resinic fractions with acceptable purity.

To study the continuous extraction of CTO by this method, the distribution data or the equilibrium extraction isotherms for both classes of acids involved must be known. Under our experimental conditions (solvent: *n*-heptane; pH 9.2; $T = 30°\text{C}$; $[\text{CTO}] < 2$ g/L; $I < 0.005$ M), it was possible to simulate the continuous extraction circuits for the separation of fatty and resinic acids from aqueous solution of CTO sodium salts with *n*-heptane by using a bench-scale countercurrent multistage plant.

To demonstrate the feasibility of the dissociation extraction process, overall distributions studies were made for both the liquid phases used. Figure 1 shows the equilibrium extraction isotherms of fatty and resinic acids fractions between aqueous solutions of the sodium salts and *n*-heptane under the conditions used.

The distribution data obtained from extraction were modeled by polynomial functions using the ENZFITTER computational program which fits the least-squares plots as can be seen in the same figure ($[\text{HF}]_o = 30.2082[\text{HF}]^4 + 0.9835[\text{HF}]$, $\sigma_a \pm 1.6800$ and $\sigma_b \pm 0.2718$; $[\text{HR}]_o = 1.0613 \times 10^{-10}[\text{HR}]^{20} + 0.0924[\text{HR}]$, $\sigma_a \pm 0.0511$ and $\sigma_b \pm 0.0223$).

The parabolic plots obtained from distribution extraction isotherms of both acidic fractions show shapes similar to the plots of other reported complex systems (17, 18) which have used the same extraction principle.

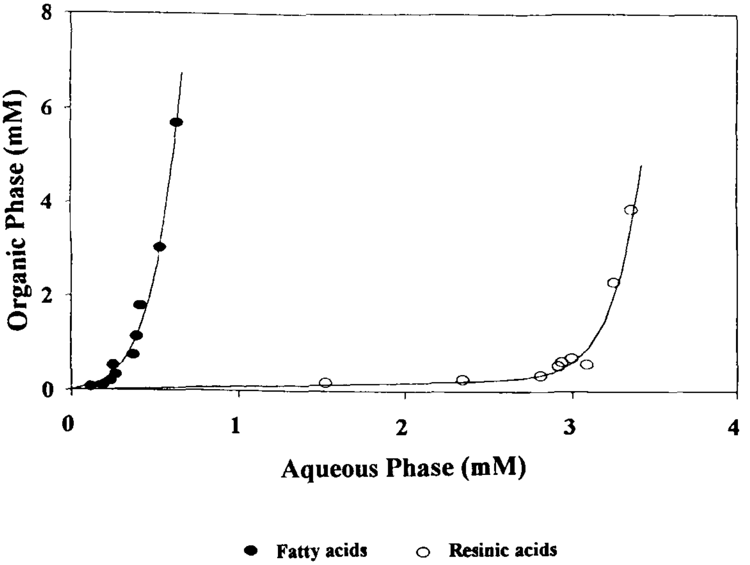

FIG. 1 Distribution extraction isotherms of fatty and resinic acidic fractions among aqueous solutions of sodium salts and *n*-heptane (T = 30°C; pH 9.2).

The differential solubilities observed are in satisfactory agreement with theoretical studies previously made, indicating higher solubility for oleic and linoleic than for diterpenic acids in organic medium under the same experimental conditions. A substantial hydrophobicity difference is seen.

Theoretical Stage Calculations

Consider a raffinate rich in resinic acids and of 99% purity (in relation to fatty acids). When optimum experimental conditions were used in accordance with systematic *batch* studies, three theoretical stages for extraction could be predicted by the McCabe–Thiele graphic method. Figure 2 shows both modeled plots obtained from distribution extraction isotherms and adequate operating lines (O/A = 7/3) to avoid emulsions. From such considerations, in which the raffinate has resinic and fatty acids concentrations of nearly 2.20 and 0.02 mM respectively, the immiscibility of both layers is negligible and theoretical stages were predicted in the usual way, among isotherm plots and operating lines adopted, with a very reasonable degree of accuracy.

Using such graphic methods, an organic extract with concentrations of nearly 0.42 and 0.35 mM for fatty and resinic acids, respectively, would be

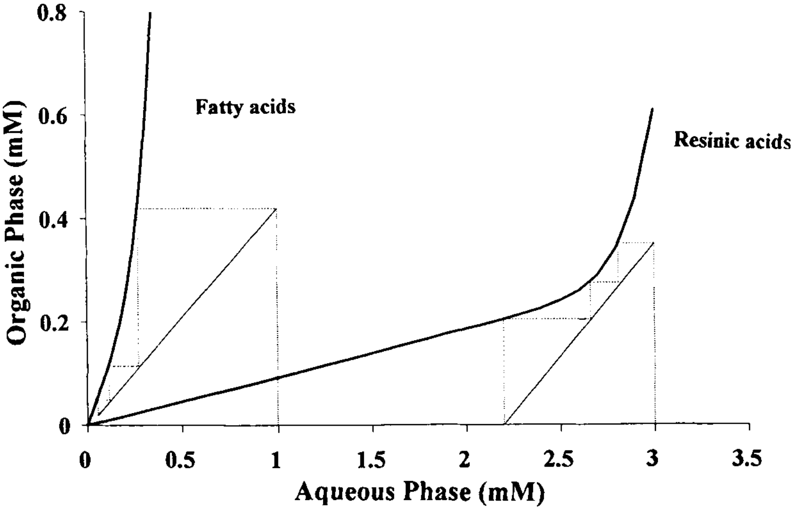

FIG. 2 Prediction of stages composition using a McCabe–Thiele diagram for continuous countercurrent extraction of fatty and resinic acidic fractions from CTO aqueous solutions of sodium salts with *n*-heptane (T = 30°C; pH 9.2; [CTO] = 1.50 g/L: [HF] = 1.00 mM, [HR] = 3.00 mM; $I < 0.005$ M; O/A = 7/3).

expected. For such compositions a washing circuit should be acceptable to recover the mass balance between both acidic fractions in the organic extract, as can be seen in Fig. 3, which also employs a McCabe–Thiele diagram. The equilibrium scrubbing isotherms of fatty and resinic acids from the organic medium show that only one theoretical stage is necessary to promote very good advantage between both acidic fractions involved, with a reasonable recovery yield, especially for resinic acids (30%). Adequate operating lines (O/A = 7/2) were used to avoid foams.

From those predictions, three theoretical stages for the extraction section (E_1, E_2, and E_3), one for the scrubbing section (W), and finally one for the stripping or backextraction section (S), including the overall regeneration of *n*-heptane in the organic circuit, will be needed to obtain good recoveries and high purities for fatty and resinic raffinates.

Multistage Continuous Extraction

After the above considerations, a continuous countercurrent extraction to recover fatty and resinic acids from CTO sodium salts aqueous solutions with *n*-heptane was employed. Figure 4 shows the process diagram

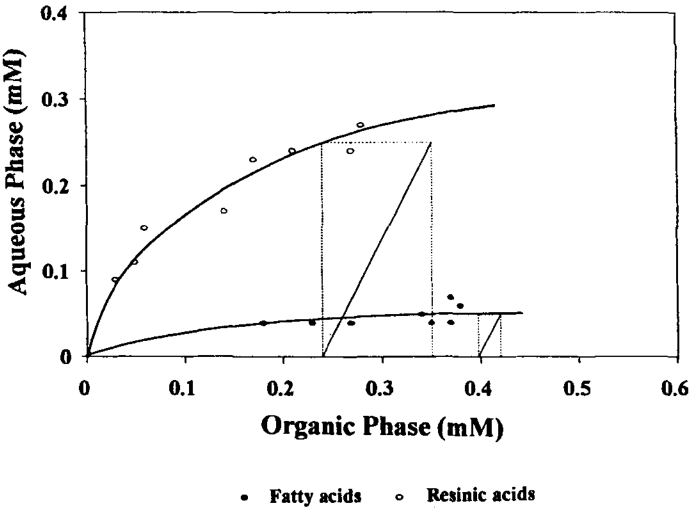

FIG. 3 Prediction of stage composition using a McCabe–Thiele diagram for continuous countercurrent scrubbing of fatty and resinic acids in *n*-heptane with a diluted aqueous solution of sodium hydroxide (T = 30°C; [NaOH] = 0.01 g/L, pH 10.50; $[HF]_o$ = 0.42 mM, $[HR]_o$ = 0.35 mM; $I < 0.005M$; O/A = 7/2).

adopted using a bench-scale mixer-settler extractors. This typical apparatus, in which the entrance for the CTO feed solution is located in the middle of the process, can be adopted to separate and purify components from each other. It is in agreement with complex refining systems adopted by several authors for rare earths, phenol isomers, penicillin purification, and also using the dissociation extraction technique (19).

Figure 5 presents a flow chart of CTO continuous extraction, showing average flow rates, pH, and compositions of both acidic fractions involved in each stage (E_1, E_2, E_3, W, and S), as well as the average streams with the purities and recoveries obtained after working for 18 hours. Different flow ratios (O/A) were adopted in all sections in order to better control the coalescence and avoid emulsions. It can clearly be seen that a raffinate with a substantially high purity fraction and containing resinic acids was obtained (96%). A corresponding fatty fraction was recovered from organic extract, which indicated a lower purity value but had a very high recovery level (92%).

A far better overall view of the extraction circuit can be observed in Fig. 6 which shows the comparison between the predicted and obtained compositional average stages of fatty and resinic acids using

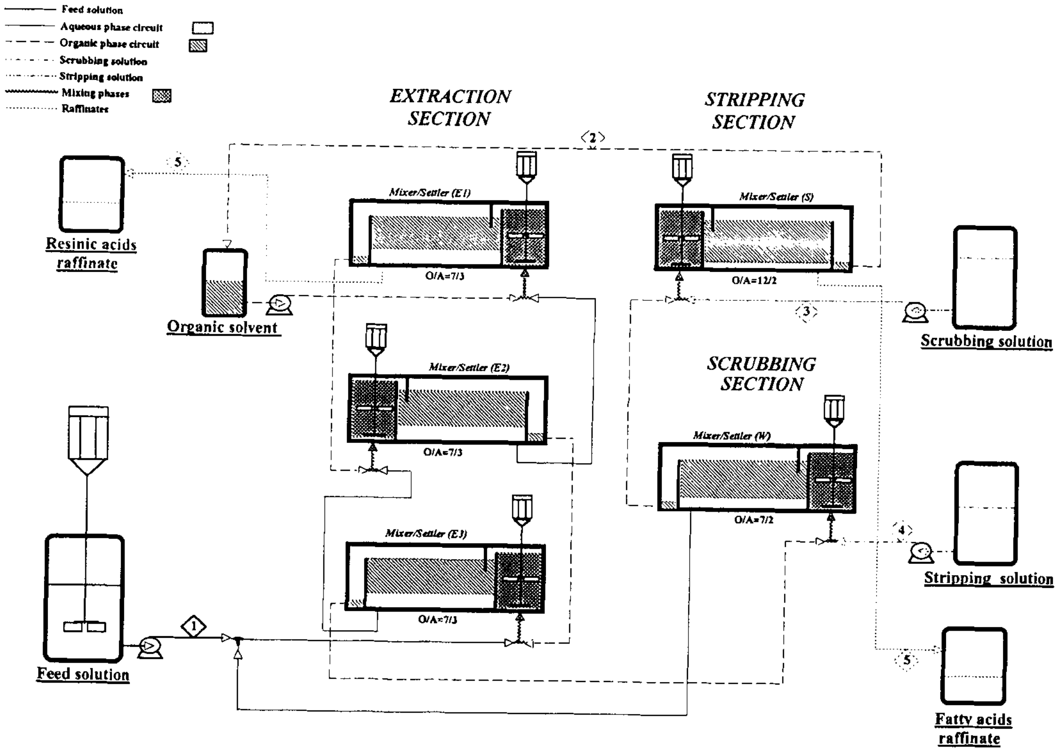

FIG. 4 Process diagram showing the apparatus used in the bench-scale multistage mixer-settler plant fo continuous extraction of CTO.

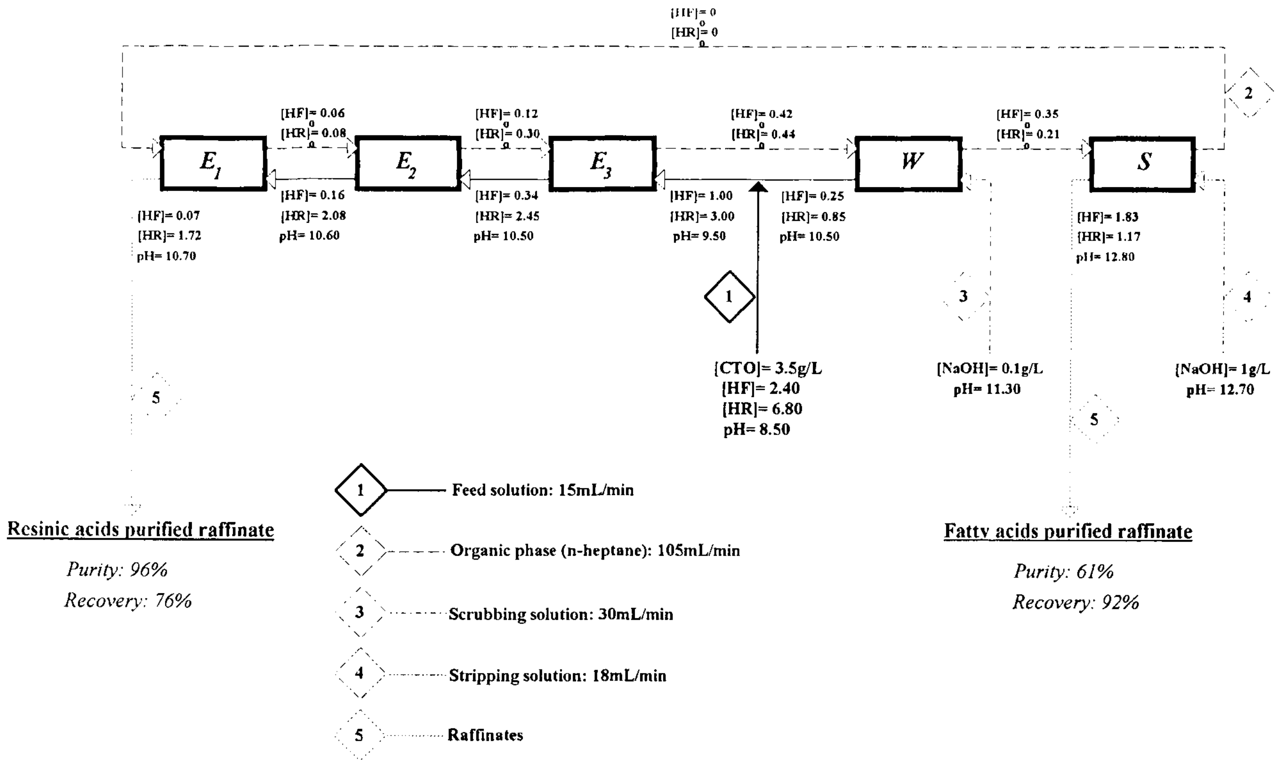

FIG. 5 Flow chart showing the average flow rates, pH, and compositions (mM) of fatty (HF) and resinic (HR) acids from a be scale multistage countercurrent mixer-settler plant of continuous extraction of CTO aqueous solution of sodium salts with *n*-hept

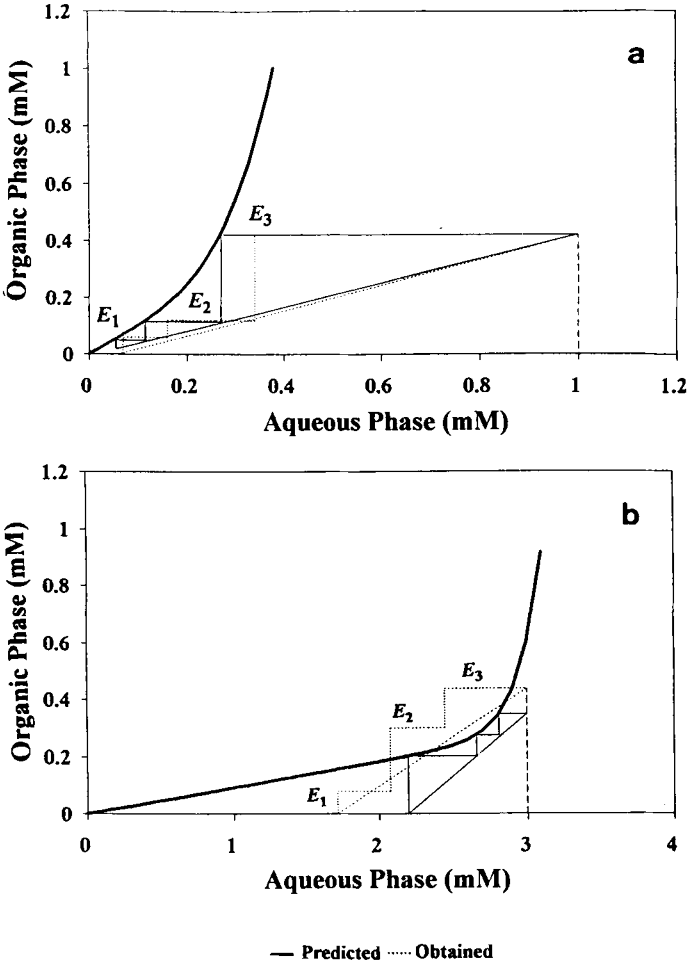

FIG. 6 Predicted and obtained average stages of composition of continuous countercurrent extraction of fatty (a) and resinic (b) acids using a bench-scale mixer-settler plant.

McCabe–Thiele diagrams. From such data the average composition of the fatty fraction obtained in each stage of extraction section approaches the expected theoretical compositions and shows high efficiencies (>80%). However, some deviations for the compositional average of the resinic fraction obtained in the corresponding stages can be observed.

These may be explained by fluctuations in the liquid circuits over the continuous system.

Figure 7 shows the scrubbing stage (*W*). It confirms that advantage was taken of the fatty and resinic acid fractions in the organic phase following the previous countercurrent extraction stages.

Finally, the stripping stage (*S*) definitely recovers the overall acidic content from *n*-heptane, for which completely regeneration in the organic circuit was obtained.

Increasing the number of stages in the extraction and scrubbing circuits, as well as using an industrial solvent, e.g., *n*-dodecane (which has characteristics more appropriate for this kind of extraction process as well as a lower cost than *n*-heptane), did not show any additional advantage in the purity of the final streams and in the recovery. Indeed, resinic fraction raffinate was always present in more than 90% purity, and higher recoveries were also observed for fatty fraction raffinate (20).

Although the results from continuous extraction showed its practicality for refining CTO from sodium salts aqueous solutions, the most important feature of our study using mixer-settler extractors is the agreement between *batch* and continuous studies. Batch studies are strongly supported by a theoretical mathematical approach (7).

The industrial scale-up of such a multistage process for refining CTO must be carefully developed in order to control all parameters. A preliminary pilot plant should be built.

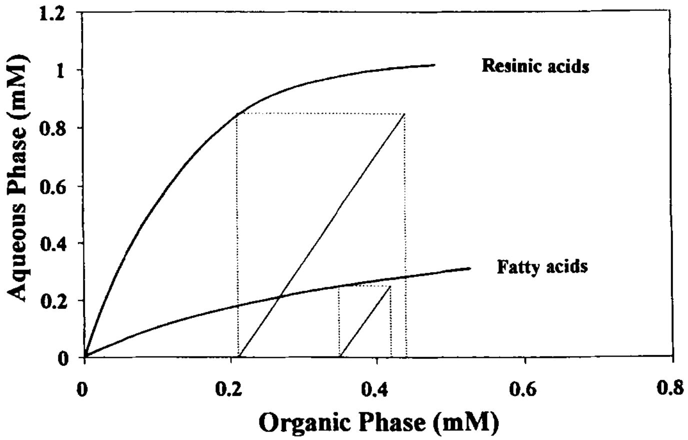

FIG. 7 Obtained average stage of composition of continuous countercurrent scrubbing of fatty and resinic acids using a bench-scale mixer-settler plant.

CONCLUSIONS

A bench-scale multistage countercurrent continuous plant using mixer-settler extractors is demonstrated to be adequate for CTO fractionation. It has high levels of purity and recovery, mainly for the resinic fraction. Its industrial feature could include the purification of fractions of distilled tall oil and tall-oil rosin usually obtained from traditional distillation under high vacuum.

No significant differences were found in the extraction and scrubbing circuits for experimental and predicted compositions, especially for fatty fraction, which supports our theoretical considerations.

Although good results were obtained for our continuous system, other aspects should be carefully studied before a scale-up in design is seriously considered.

ACKNOWLEDGMENTS

The author wishes to thank Prof. J. L. C. Pereira for supervising, PORTUCEL SA for the crude tall-oil samples, Eng. Carlos Nogueira from INETI-Lumiar for technical assistance, and "Programa Ciência" (Junta Nacional de Investigação Cientifica e Tecnológica) for a scholarship.

NOTATION

[NaOH]	sodium hydroxide concentration
[CTO]	crude tall-oil concentration
[HF]	fatty acids concentration
[HR]	resinic acids concentration
E	extraction stage
I	ionic strength
O/A	organic and aqueous flow ratio
N	number of stages
T	temperature
σ	standard deviation

Brackets and Subscripts

HF	fatty acids
HR	resinic acids
$1, 2, 3$	stage number
o	organic phase
a	higher-order term
b	first-order term

REFERENCES

1. J. M. F. Nogueira, J. L. C. Pereira, and P. Sandra, *J. High Resolution Chromatogr.*, 18(7), 425–432 (1995).
2. E. E. McSweeney, H. G. Arlt Jr., and J. Russell, *Tall-Oil and Its Uses—II*, Pulp Chemicals of Association, New York, NY, 1987.
3. J. Drew and M. Propst, *Tall-Oil*, Pulp Chemicals Association, New York, NY, 1981.
4. J. M. F. Nogueira, *Sep. Sci. Technol.*, *31*(17), 2307–2316 (1996).
5. R. Lofthouse, *Proceedings of International Naval Stores Meeting*, Pulp Chemicals Association, Vienna, Austria, 1992.
6. R. W. Cusak and D. Glatz, *Chem. Eng.*, *2*, 66–76 (1991).
7. J. M. F. Nogueira, *Sep. Sci. Technol.*, *31*(19), 2685–2703 (1996).
8. M. M. Anwar, C. Hanson, A. N. Patel, and M. W. T. Pratt, *Trans. Inst. Chem. Eng.*, *51*, 151–158 (1973).
9. G. M. Ritcey and A. W. Ashbrook, *Solvent Extraction: Principles and Applications to Process Metallurgy, Part II*, Elsevier, Amsterdam, 1984, pp. 172–206.
10. P. A. Schweitzer, *Handbook of Separation Techniques for Chemical Engineers*, McGraw-Hill, New York, NY 1979, pp. 283–342.
11. T. C. Lo, M. H. I. Baird, and C. Hanson, *Handbook of Solvent Extraction*, Wiley-Interscience, New York, NY, 1983, pp. 583–591.
12. J. M. F. Nogueira, "Separation of Crude Tall-Oil Components," Ph.D. Thesis, 1995, University of Lisbon, Portugal.
13. "Standard Methods of Testing Tall-Oil, ASTM D 803," *Annual Book of ASTM Standards*, Philadelphia, 1988. p. 06.03.
14. "Standard Methods for Resinic Acids in Rosin by Gas Chromatography, ASTM D 3008-72," *Annual Book of ASTM Standards*, reproved 1986.
15. G. M. Ritcey and A. W. Ashbrook, *Solvent Extraction: Principles and Applications to Process Metallurgy, Part II*, Elsevier, Amsterdam, 1984, pp. 1–10.
16. J. M. F. Nogueira and J. L. C. Pereira, *Fresenius J. Anal. Chem.*, *350*, 379–383 (1994).
17. T. C. Lo, M. H. I. Baird, and C. Hanson, *Handbook of Solvent Extraction*, Wiley-Interscience, New York, NY, 1983, pp. 612–614.
18. M. M. Anwar, S. M. T. Cook, C. Hanson, and M. W. T. Pratt, *Proceedings of Solvent Extraction Conference (ISEC) Vol. 2*, Canadian Institute of Mining and Metallurgy, Toronto, Canada, 1977, pp. 671–676.
19. R. W. Cusak, and D. Glatz, *Chem. Eng.*, *4*, 112–119 (1991).
20. J. M. F. Nogueira and J. L. C. Pereira, *Proceedings of International Solvent Extraction Conference (ISEC), Vol. 2*, SCI, University of York, UK, 1993, pp. 1088–1094.

Received by editor August 26, 1996
First revision received March 1997
Second revision received April 1997