PN-ABA-566

AGENCY FOR INTERNATIONAL DEVELOPMENT
WASHINGTON, D.C. 20523

DATE: 4/15/88

MEMORANDUM

TO: AID/PPC/CDIE/DI, room 209 SA-18

FROM: AID/SCI, Victoria Ose VO

SUBJECT: Transmittal of AID/SCI Progress Report(s)

Attached for permanent retention/proper disposition is the following:

AID/SCI Progress Report No. 7.143
PR #1

Attachment

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CENTRO DE QUÍMICA ESTRUTURAL
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INSTITUTO SUPERIOR TÉCNICO
1096 LISBOA-CODEX PORTUGAL

PN-ABA-566

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7.143

PROJECT Nº: 936-5542

PROJECT TITLE: "SUPERCRITICAL - FLUID EXTRACTION OF NATURAL AND BIOLOGICAL PRODUCTS"

GRANT Nº: DPE-5542-G-SS-7048-00

PROJECT OFFICE: S&T / SCI

OBLIGATION Nº: 736 1213

PRINCIPAL INVESTIGATOR: MANUEL NUNES DA PONTE

GRANTEE: CENTRO DE QUÍMICA ESTRUTURAL
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Rec'd in SCI

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FINANCIAL REPORT N.1/88

From 08/20/87 to 02/19/88

The total expenditure during the 1st semester of this project is summarized below:

i) Item: "Equipment"	
Gas compressor Newport Scientific	$12,398
High-pressure fittings	$1,586
Metering pump Lewa ELM-1V	$4,844
ii) Item: "Materials & Reagents"	$2,681
iii) Item: "Overheads"	$4,302
TOTAL	$25,811

A more detailed description of the purchases shown above can be found in our Voucher N. 1/88.

In addition to these aquisitions, we have started the process to order other pieces of equipment, namely pressure gauges, mass flowmeter, and back-pressure regulators, which we will need for our apparatus.

The expenses described above were paid in Portuguese Escudos and were converted to US $ using the exchange rate 1US $=137.92, as of February 26,1988.

February 26, 1988

Manuel Nunes da Ponte

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PROGRESS REPORT Nº 1

Period from 20/AUG/87 to 19/FEV/88

This period corresponded to the start-up of the project.

Activities were centered on four main areas:

i) Training program and development of collaboration.

ii) Solubility measurements on eucalyptus oil components.

iii) Design and construction of countercurrent extraction apparatus.

iv) Extraction from fermentation broths - redefinition of suitable systems.

Progress achieved in each of these areas is described below.

i) Training program and development of collaboration

Dr. Susana Barreiros, one of the investigators in this project, is currently spending one year at the University of California, Berkeley, in Prof. Prausnitz's group, on a post-doctoral leave from the New University of Lisbon. Scientific collaboration with Prof. Prausnitz's group was part of our proposal, but Dr. Barreiros stay is being funded by Portuguese sources. She is studying supercritical carbon dioxide as a solvent in enzymatically catalysed reactions. The experience obtained in this work will be very valuable in the development of part of our project aiming at extraction from fermentation broths.

A new graduate student has been added to this project, Margarida Gonçalves, who has obtained a grant from Portuguese sources. She is developing an apparatus for solubility measurements with lactic acid, as described in iv) below.

ii) Solubility measurements on eucalyptus oil components

In our proposal, we described (pp 15 - 16) some preliminary measurements of solubility of limonene, one of the main components of eucalypyus oil, in supercritical carbon dioxide. Since then, the existing solubility apparatus was improved, following some of the modifications in the proposal:

a) A manual piston liquid pump, that can deliver pressures up to 5000 psi, is now used to feed carbon dioxide into the cell. This considerably improved the control and range of working pressures.

b) The sample collection system was changed. The precipitated solute is now deposited directly in a glass trap, immersed in ice, and its quantity measured by weighing.

With this modified apparatus, extensive vapor-liquid equilibrium measurements were performed for carbon dioxide + limonene and carbon dioxide + cineole, at 40, 45 and 50ºC (limonene and cineole are the main components eucalyptus oil). The obtained results are shown in Figs. 1 - 3. These data show that previously published results on the solubility of terpenes in supercritical carbon dioxide[1] are wrong. Figure 4 compares our VLE results on CO_2 + limonene at 40ºC with the solubility results given in reference (1). These are obviously in error above the critical pressure of the mixture, where a solubility cannot be defined, because limonene and carbon dioxide are completely miscible.

As a first step in the thermodynamic modeling of these systems, the Peng-Robinson equation was used. Calculated values of vapor-liquid equilibrium compare well with our experimental results, as shown in figures 1-3.

Measurements on the ternary system CO_2 + limonene + cineole are now in progress. This is an important part of the study, and will establish whether or not pure supercritical CO_2 can effectively separate cineole from limonene.

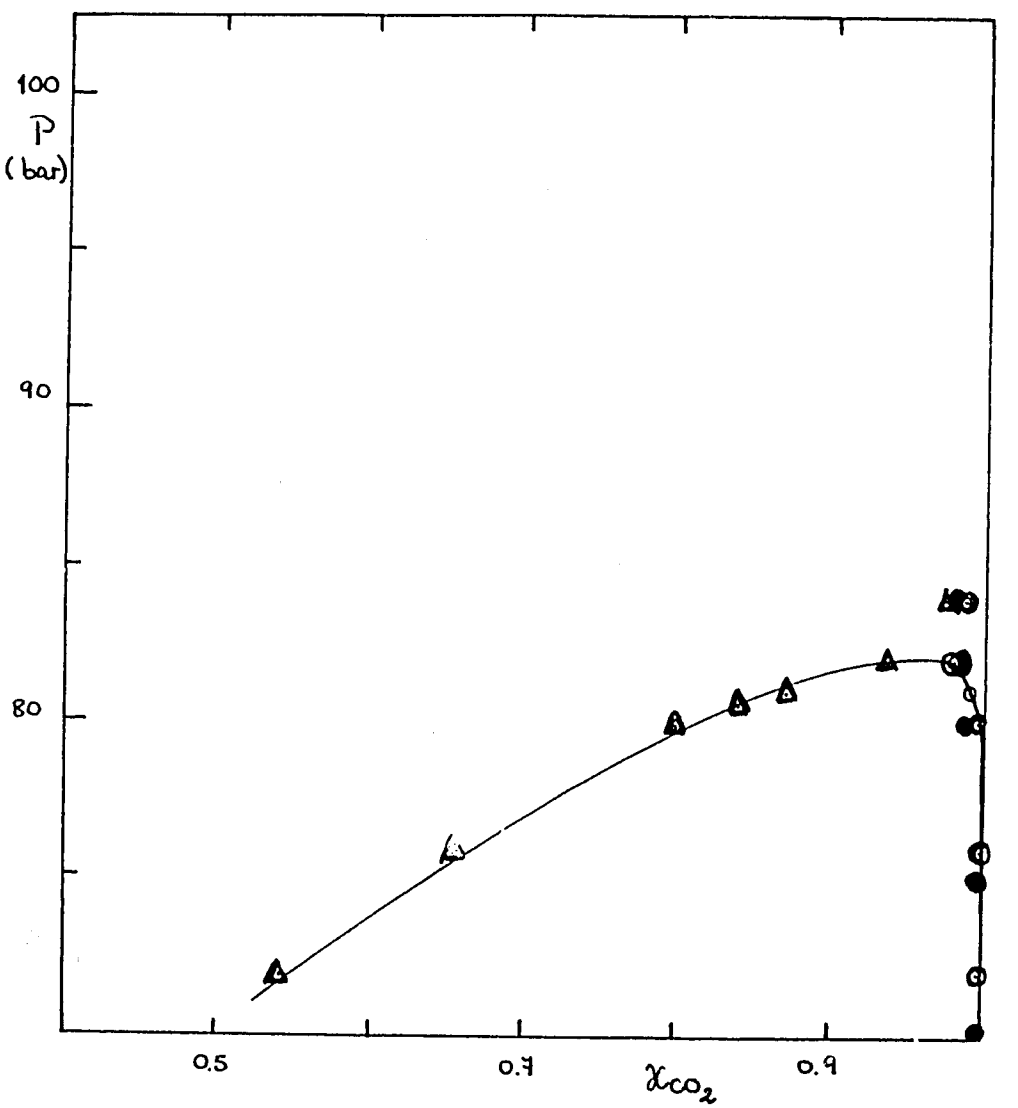

Figure 4 - Vapor-liquid equilibrium measurements on limonene + CO_2 .
⊙ vapor, △ liquid, this work; ● solubility measurements of Stahl and Gerard[1].

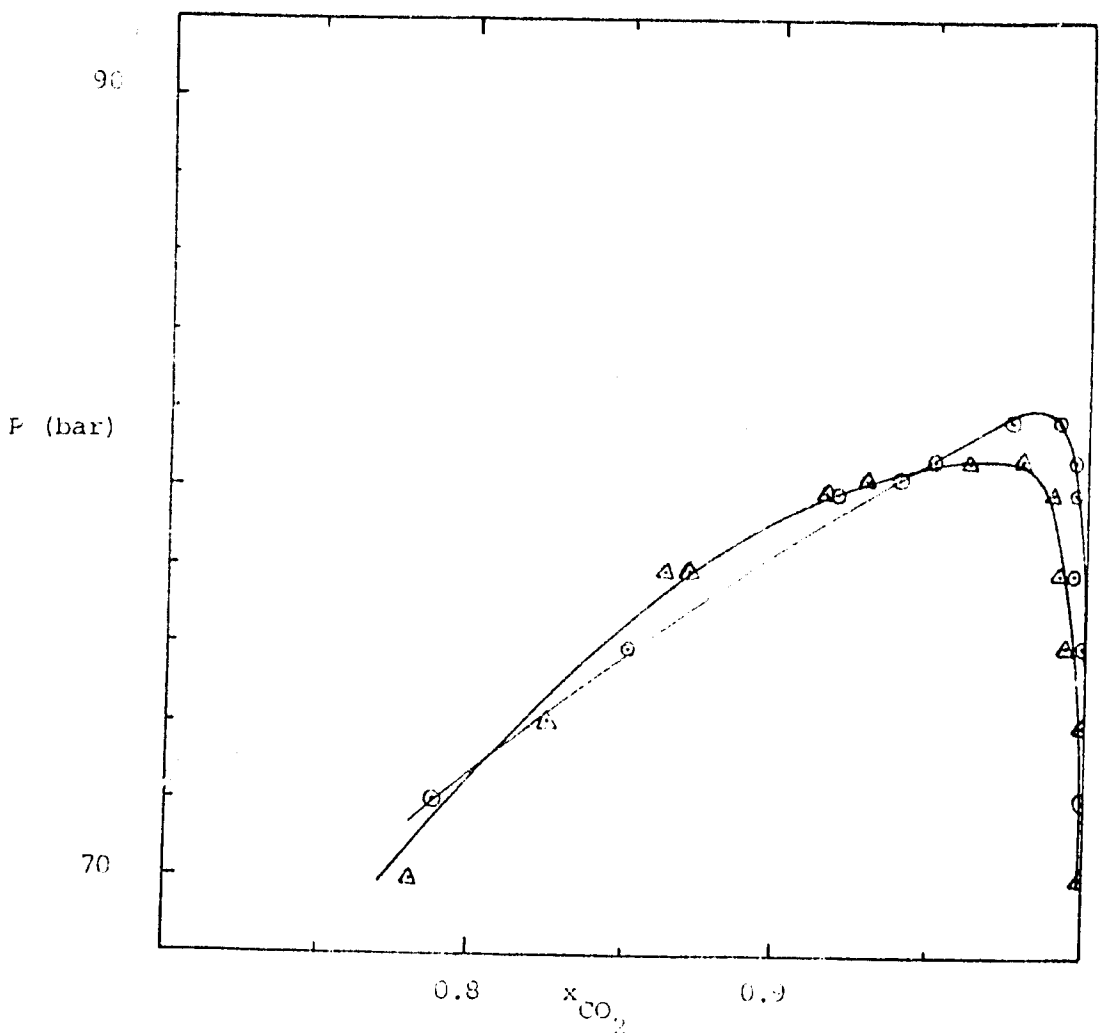

Figure 1. Vapor-Liquid Equilibria for the systems carbon dioxide + limonene (⊙) and carbon dioxide + cineole (△) at 313 K.

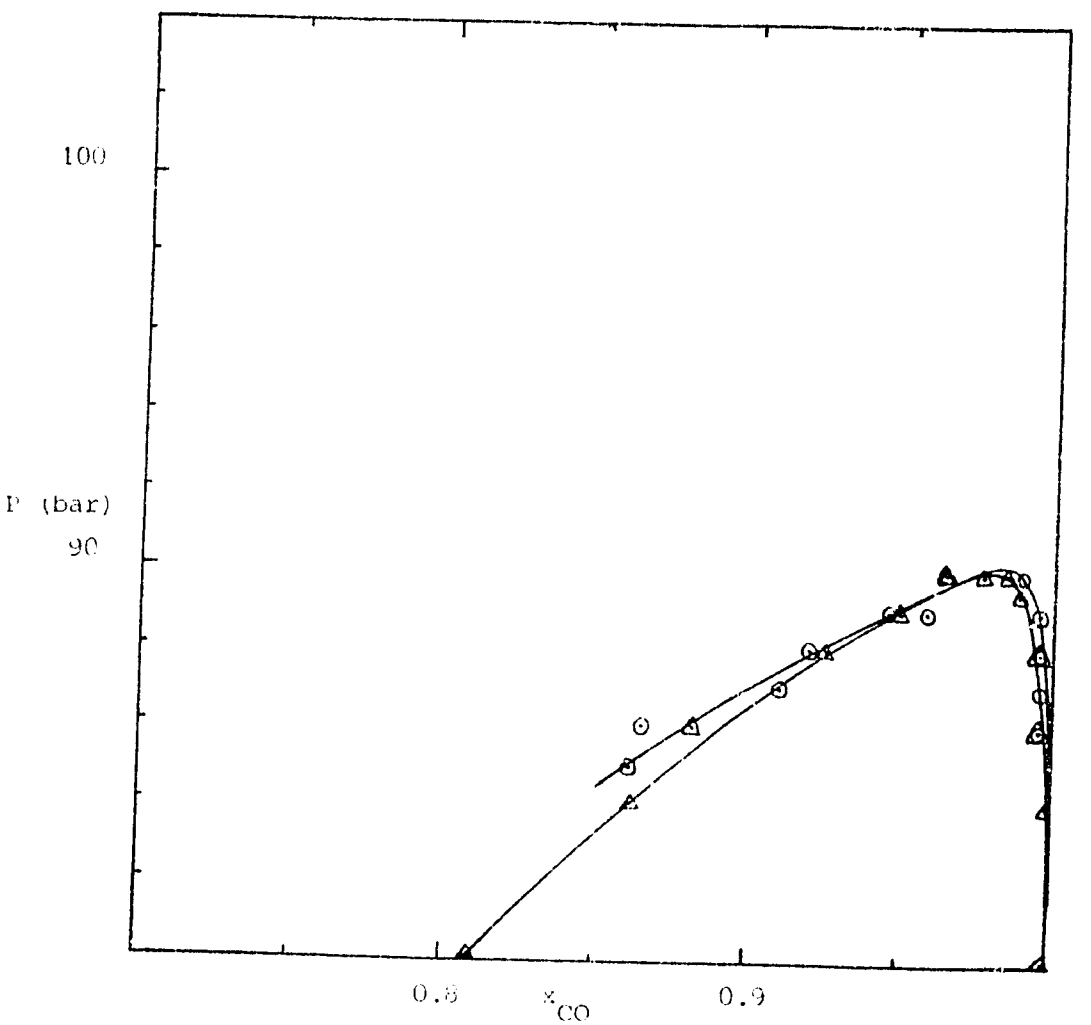

Figure 2. Vapor-Liquid Equilibria for the systems CO_2+limomene (⊙) and CO_2+cineole (△) at 318 K.

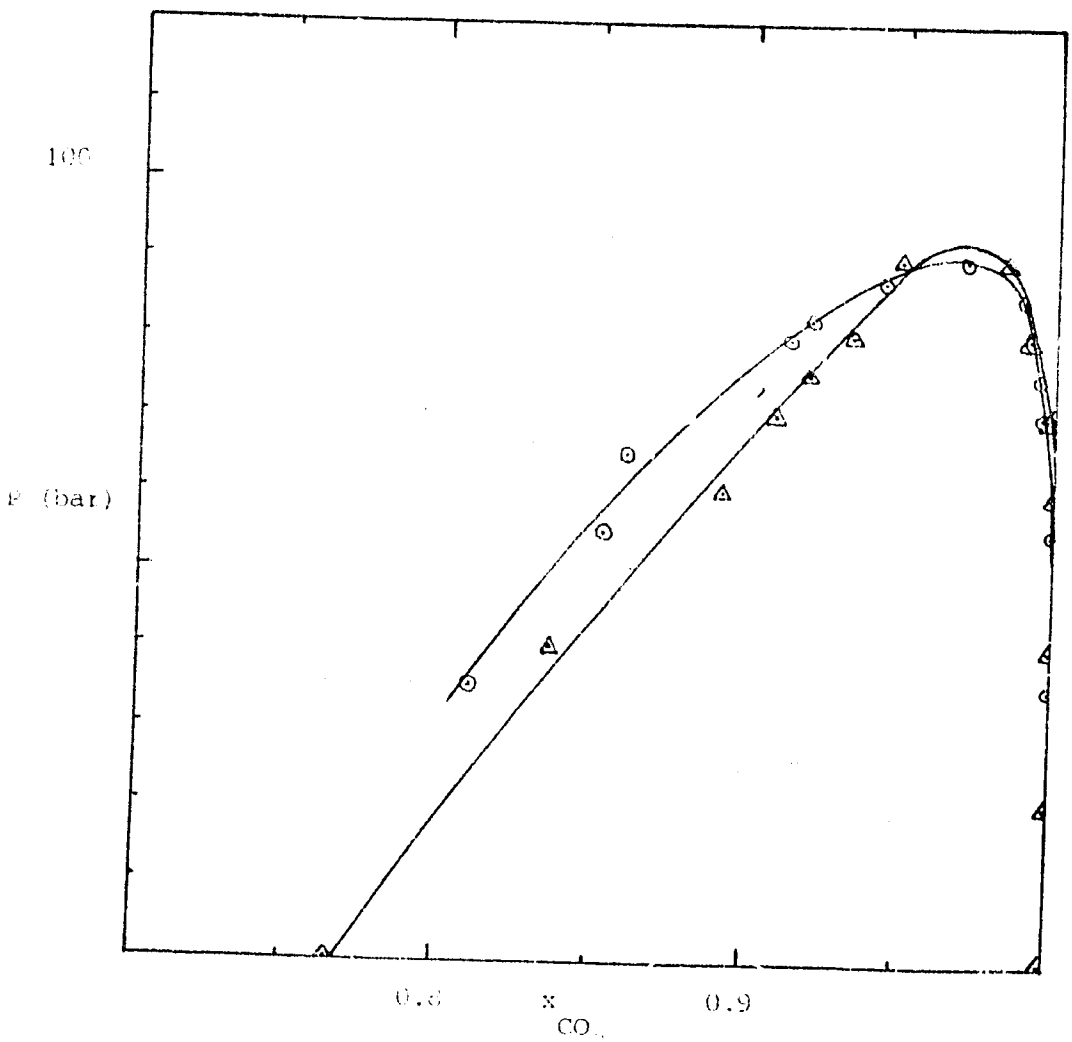

Figure 3. Vapor-Liquid Equilibria for the systems CO_2+limonene (⊙) and CO_2+cineole (Δ) at 323 K.

iii) Design and construction of countercurrent extraction apparatus

We have completed the design and construction of the extraction columns and heat exchangers for the apparatus described on pp. 18 - 21 of our proposal. Selection and purchase of the necessary equipment is in progress. A compressor for carbon dioxide and a high-pressure metering pump for the liquid feed were already bought. Purchase orders for back-pressure regulator, mass flowmeter, pressure gages, and miscellaneous high pressure equipment have been submitted or are being prepared.

iv) Extraction from fermentation broths

One of the goals of this project was the study of extraction of propionic acid from a fermentation broth. However, it has recently been brought to our attention that a similar study is being carried out at M.I.T., by Cooney and Willson[2]. To avoid duplication of efforts, we searched for an alternative. In the Biotechnology Laboratory of the New University of Lisbon, where the study of propionic acid fermentation by gram positive Propioni bacterium is being carried out, there is a parallel study on lactic acid fermentation.

Lactic acid is a more polar molecule than propionic acid. This makes it less likely to be effectively extracted by supercritical carbon dioxide. However, lactic acid is a more valuable product, and existing separation processes from fermentation broths are complicated and expensive .

The economic incentive for a new extraction process is therefore much stronger than for propionic acid. However, literature values [3] indicate that lactic acid is slightly soluble in liquid carbon dioxide. There is therefore a possibility that supercritical CO_2 might be an adequate solvent for extraction purposes, and we decided to initiate a program of solubility measurements. As lactic acid aqueous solutions are very corrosive, it is necessary to use stainless steel (AISI 316) in all equipment pieces in contact with it and a new apparatus is in construction.

We believe that the project actual accomplisments during this period compare quite well with the goals we have established in our proposal for the same period (p.23). The development of the solubility apparatus is completed and measurements of the solubilities of eucalyptus oil components has started (step 1). The design and cons-

truction of the extraction columns is well under way and the assembly of the apparatus is in progress (step 3).

REFERENCES

(1) E. STAHL, D. GERARD, Perfumer & Flavorist, 1985, 10, 29.

(2) R.C. WILLSON, C.L. COONEY, A.I.Ch.E. Meeting, New York (1987).

(3) W.G. SCHULTZ, J.M. RANDALL, Food Technology, 1970, 24, 1282.