PN-ABK-238
75204 8.051

FINAL REPORT

Covering Period: October 1, 1988 to August 30, 1991

Submitted to the Office of the Science Advisor
U.S. Agency for International Development

UTILIZATION OF HYDROCARBON PRODUCING PLANTS NATIVE IN ARID AREAS

Principal Investigator: Dr. Sara Gnecco
Grantee Institution : University of Concepción

Collaborator : Dr. Attila Pavlath
Institution : Western Regional Research Center
U.S.D.A. Albany C.A. U.S.A.

Project Number : 8.051
Grant Number: DPE-5542-G-SS-8029-00

A.I.D. Grant Project Officer: Dr. Alberto Sabadell

Project Duration: October 1, 1988 August-30, 1991

Rec'd in SCI OCT 7 1991

TABLE OF CONTENTS

		Page
I.	Executive Summary	2
II.	Research Objectives	3
III	Methods and Results	6
IV	Impact Relevance and Technology Transfer	22
V	Project Activities/Outputs	22
VI	Project Productivity	24
VII	Future Work	25
VIII	References	25

I.- EXECUTIVE SUMMARY

Oil and hydrocarbon producing plants, growing in arid regions, are promising candidates as sources of renewable fuels and chemicals. Theirs extracts are potential starting material for energy rich fuels and/or valuable chemicals through pyrolytic reactions. However, in order to utilize economically these plants,it is necessary to study the effect of various catalysts on the pyrolysis and identify the most promising ones, as a first step to develop the related technology.

To asses the suitability of obtaining fuels, extracts of chilean latex bearing plants were pyrolyzed catalytically. Zeolitic catalysts were chosen because they have shown to be more active and shape selective than conventional catalysts in the conversion of heavy hydrocarbons and also of methanol to fuels.

Serie of zeolites, faujasite-type, with different acidity and containing metals suitable for cracking, isomerization, dehydration and carbonyl reduction processes were synthesized and characterized. CH_2Cl_2 extracts from selected species and theirs main components were pyrolyzed whith the synthetized catalysts and ZSM-5, the zeolitic Mobil's catalyst, under different experimental conditions. Conversion degree and quality of the products were estimated by means of thermogravimetry (TG), differential scanning calorimetry (DSC), gas chromatography (GC) and combustion heat.

On the basis of the TG and DSC results, the best conditions for the catalytic pyrolysis would be: temperature 400°C and high heating rate. Most of the catalysts sped up the process of pyrolysis and enhanced the present of conversion of the substrates. According the TG analysis, conversions from 69.5% to 88.5% were obtained for extracts. The estimated combustion heat for the pyrolytic products ranged from 6.84 to 8.81 Kcal per gram of extract.

Regarding the percentage of conversion, the heat of combustion and the relative composition of volatile pyrolytic products, the catalysts that seemed to direct more efficiently the pyrolysis of the extracts of hydrocarbon producing plants to mixtures with interest as fuels or industrial chemicals, besides ZSMS, were: Mo(2) NaY, Co(1) Mo(0.5)NaY and H(40)NaY.

Therefore extracts of hydrocarbon producing plants native in chilean arid lands could be upgraded using the selected catalysts and conditions of pyrolysis. Utilizing as starting point or results, suitable technology has to be developed, first at laboratory scale then at pilot level.

II.- RESEARCH OBJECTIVES

In recent years there has been considerable interest in developing renewable resources as alternatives to petroleum based substances and various groups have actively pursued a multidisciplinary approach to identify and establish new crops for this purpose (1-4). Arid lands, presently underused or completely unsuitable for conventional agriculture, offer the greatest opportunity. The most economically important desert plants are those that produce various materials with no or little contents of oxygen, e.g. rubber, paraffins, waxes, etc. Although they have a slower overall growth rate than conventional crops, these plants allow increased water economy by producing a greater energy content per unit of dry weight biomass (5).

For many years our group has studied, as possible chemical resources, various species of the Euphorbiaceae, Compositae, Zygophyllaceae and Apocynaceae families, growing in chilean arid zones, with the aim of identifying new energy crops. Extraction and characterization techniques of hydrocarbons and carbohydrates have been developed and preliminaries studies on pyrolysis and fermentation of extracts from these plants have been done (6-8). We found that some of the species studied were promising renewable resources for hydrocarbons and/or carbohydrates: Euphorbia lactiflua, Tessaria absinthioides, Euphorbia copiapina, Baccharis santelices, Perezia atacamensis. The apparent protein contents of some of these species are up to 10%. Also the roots of E.copiapina form tubers, with a high content of starch (40% on dry bases). Thus, these species should be studied as multiuse botanochemical crops offering potential for combining the production of fuels, industrial raw material and food, with increased overall productivity.

The extracts from these plants, with high H/C ratio and low S and N contents, are potential starting materials for energy rich fuels and/or valuable chemicals through pyrolytic reactions. However, we must study the effect of various catalysts on the composition of the pyrolytic products and identify the the most promising ones, in order to utilize economically these plants. The development of an efficient pyrolytic method that converts extracts from latex bearing plants into valuable fuels and chemicals would provide a great help for the economy of, and for the improvement of chemical industry in many developing nations.

Most of the work on the pyrolytic reactions of biomass were carried out with the carbohydrates. There is very little known on the influence of catalysts, pre-

teatments and other reaction conditions on the compounds obtainable through the pyrolysis of the extracts from latex producing plants. These reactions include: cracking, dehydration, isomerization, decarboxylation, depolymerization and carbonyl reduction.

For the conversion of heavy hydrocarbons to fuels, the most utilized zeolite catalyst is 80% amorphous alumina as matrix and 15-20% of zeolite, generally ultrastable Y-type. This catalyst is 10^3-10^4 times more active than amorphus conventional catalysts, e.g. SiO_2/Al_2O_3 (9). Zeolites also results in secondary reactions, not observed in amorphous catalysts, that increase the octane number, e.g. conversion of naphthenes and oleffins to aromatics by means of hydrogen transfer thus they are not only more active than conventional catalysts, but also more selective.

The Mobil ZSM-5 pentasil-type zeolitic catalyst designed for conversion of methanol to gasoline, was utilized for the conversion of vegetal extracts to fuels (11, 12). The pore size of pentasil zeolites is 5.9 Å and the central cavity size is 9.0 Å. Therefore, there could be shape selectivity towards products, reactives and transition state (10). Thus, the main advantages in utilizing zeolitic instead of conventional catalysts for cracking are: higher conversion to gasoline-type of compounds, aromatics and paraffins and lower conversion to gaseous hydrocarbons, coke and oleffins.

It is difficult to taylor-make "a priori" a catalyst for all the rypes of reactions that take place in converting biomass extracts to valuable chemicals. However, we theorize that owing to their acidic and structural properties such as larger pore size and central cavity size than those of ZSM-5, thermostable zeolitic faujasites would be appropiate. Some bifunctional catalysts, e.g. Pt/faujasite, would be also good candidates to improve reduction of carbonyl groups and to diminish the formation of coke which deactivates the catalyst.

Overall Aims of the project:

a. To develop an efficient method for converting extracts from hydrocarbon producing plants, native in arid areas, to energy rich fuels and/or valuable chemicals.

b. To establish a multidisciplinary research approach in a field of great relevance at international level utilizing an expert group of scientists, both

in Chile and USA.

Specific Project Objectives:

a. To convert, through pyrolytic reactions, mostly such polymer components of extracts from hydrocarbon producing plants as polyisoprene, n-paraffins and resins, to lower molecular weight materials with high hydrogen to carbon ratio and with high value as fuels or chemicals.

b. To determine the composition of products forming during these conversion reactions, and the change in composition, as a function of reaction conditions as temperature, heating rate, catalysts.

III.- METHODS AND RESULTS

1.- Extraction, fractionation and analysis

Plant species were collected from the wild, in the North of Chile (III and IV Regions). Voucher specimens were kept at the University of Concepción Herbarium (Conc.). Samples of latex from Euphorbia lactiflua were collected by tapping wild plants.

Dried milled samples were extracted in a Soxhlet apparatus with CH_2Cl_2 for 40 hours. After the evaporation of the solvent, the material obtained (CH_2Cl_2 Extract) was extracted with acetone to obtain acetone-soluble and acetone-insoluble fractions. Representative fractions were characterized by quantitative analysis, IR, ^1H and ^{13}C NMR spectroscopy, TLC and GC (6). Results are given in Table 1.

TABLE 1

YIELD, MOLAR RATIO C/H OF REPRESENTATIVE FRACTIONS AND POLYMERIC HYDROCARBON TYPE FROM SOME CHILEAN SPECIES.

SPECIES	CH_2Cl_2 EXTRACT		ACETONE-INSOLUBLE FRACTION		POLYMERIC HYDROCARBON TYPE[c]
	YIELD[a]	C/H RATIO[b]	YIELD[a]	C/H RATIO[b]	
E.LACTIFLUA	10.80	0.52	2.90	0.48	NR, WAXES
E.COPIAPINA	11.70	0.57	3.10	0.51	NR[d], WAXES
C.ODORIFERA	4.50	0.54	2.20	0.48	NR[d], WAXES
C.SALICIFOLIA	5.30	0.55	1.60	0.49	NR[d], WAXES
T.ABSINTHIOIDES	7.40	0.57	1.32	0.52	WAXES

a. Given as a percentage of plant dry weight; average value of extracts from 2 or 3 plant samples.

b. C/H molar ratio calculated from quantitative analysis data.

c. NR = Natural rubber (cis-1,4-polyisoprene) identified by spectroscopic data.

d. Traces.

2.- Isolation and Characterization of main components.

a.- n-Paraffins.

Acetone - insoluble fractions were refluxed in a suspension of activated carbon, Johns-Manville cellite (1 g. each w/w) and hexane (200 ml), fil-

tered and dried to obtain the fractions of refined hydrocarbons which were analyzed by IR, ^{1}H NMR, ^{13}C NMR, and GC (3).

NMR and IR spectra of refined hydrocarbons from different species revealed almost exclusively the presence of n-paraffins. The identification of hydrocarbons was carried out by the comparison of RRt data with those of authentic standards. The results revealed the presence of n-alkanes mixtures with chain lenghts varying from n-nonadecane (n-C_{19}) to n-tritriacontane (n-C_{33}). In the mixtures, n-heptaeicosane (n-C_{27}), n-nonaeicosane (n-C_{29}) and n-hentriacontane (n-C_{31}) were the dominant alkane components. Results are given in Table 2.

b.- Rubber

Fresh latex from E.lactiflua was mixed with C_2Cl_4. After removing the azeotrope, the solid was dried at 50°C for 12 hours. Dry latex was dissolved in CH_2Cl_2, then filtered, and the solution was added drop by drop to methanol. The precipitate was centrifuged, dried in a vacuum oven at 50°C for 2 hours and weighed, the yield was 8.05% in dry weight basis. The characterization was done by IR, NMR spectroscopy (^{13}C and ^{1}H) and TLC. All the data obtained agreed with those given in literature for cis-1,4-polyisoprene.

c.- Resins.

Resins isolated through succesive fractionation of dry latex from E.lactiflua and CH_2Cl_2 extract from C.odorifera were characterized by I.R., ^{13}C NMR and TLC with standards (1). The main components were: sterols (B-sitosterol-type), fatty alcohols (oley-type), fatty acids (oleic-type).

3.- Preparation and Characterization of Catalysts

Series of HNaY, MNaY and M_1M_2NaY (M = Pt, Ni, Co, Mo) zeolites were prepared by impregnation or partial sodium exchange of a NaY zeolite faujasite-type (Linde, Si/Al = 2.4) with NH_4^+ or suitable metalic ions. The degree of ionic exchange was determined by atomic absorption sodium analysis in the filtrate. Dehydration, deamination and dehydroxilation were carried out at 110°C, 250-520°C and 480-550° respectively. Reduction of PtNaY catalysts was carried out with H_2 at 520°C (13-16).

TABLE 2

YIELD AND MOLAR RATIO C/H OF REFINED HYDROCARBONS FRACTIONS FROM SOME CHILEAN EUPHORBIACEAE SPECIES. N-ALKANES FOUND IN THESE FRACTIONS.

Species	Ref.Hydroc. yield[a]	C/H ratio[b]	Composition (%)[c]								
			C_{21}	C_{23}	C_{25}	C_{27}	C_{29}	C_{30}	C_{31}	C_{32}	others
E.lactiflua	1.8	0.45	11	2	6	26	4	1	-	-	C_{19} = 22 C_{20} = 20
E.copiapina	1.1	0.44	-	-	1	1	7	1	85	1	C_{19} = 2
C.odorifera	1.4	0.45	-	-	-	58	41	-	-	-	-
C.salicifolia	1.3	0.44	-	-	-	98	-	-	-	-	-

a: Percent on dry plant weight basis

b: C/H molar ratio calculated from quantitative analysis data

c: Percent obtained by measurement of peak areas, expresed as a percentage of the sum of the peak areas of all compounds lying between n-C_{19} and n-C_{33}. Compounds detected in percentage less than 1% are not given.

The crystallinity of the exchanged zeolites was determined by X-ray diffraction using the powder method (14). The specific areas of the prepared zeolites were determined by the absorption method of N_2. The analysis were performed in a volumetric BET conventional equipment at-196°C (15). The number of acid centers and their relative strengths were determined by a potentiometric method (16). Results are given in Table 3.

4.- Thermochemical transformations.

a.- Preparation of samples sustrate/catalyst.

Samples were prepared by adding a suitable mass of each catalyst, finely ground, to a CH_2Cl_2 solution of each sustrate (n-paraffins, rubber, resins). The solvent was evaporated at 50°C, under vacuum in a micro-semimicro rotatory evaporator. The dried solid was homogenized in a small agatha mortar, heated overnight at 40°C, and put in a dessicator under vacuum for 2 hours before analyzing.

Samples with sustrate/catalyst ratio 1/1, 7/3 and 9/1 (wt/wt) prepared.

b.- Thermogravimetric analysis.

C.Odorifera n-paraffins, *E.lactiflua* polyisoprene and *E.copiapina* resins were selected as model substrates. The rate of weight loss, and the weight of the residue of each substrate, catalyst , and mixtures S/C, were determined in a TG under N_2. The samples were sealed in aluminium pans with a pinhole on top for the escape of volatiles. A temperature range of 50-550°C and heating rates of 20, 40 and 80 degrees/min were used. The results for samples S/C = 1/1 (wt/wt) and S/C = 7/3 (wt/wt) are given in Tables 4 and 5. Percents of total weight loss (substrate + catalyst) were corrected and are given in percent of weight loss of the substrate.

Results for samples S/C = 9/1 (wt/wt) are not given because were not reproducible. This may be due to the fact that it is very difficult to obtain homogeneous samples with this ratio, and a small error in the quantity of catalyst may cause a large error in the results.

For a given mixture sustrate/catalyst, heated at the same rate, the comparison of results with those for mixtures S/C = 1/1 wt/wt does not showed a clear and definite trend. In some cases T inf, % WL inf and % WLf for mixtures 7/3 were higher and in other cases were lower than those for mixtures 1/1.

TABLE 3

CHARACTERISTICS OF THE PREPARED ZEOLITES AND ZSM-5

PREPARATION METHOD	DEGREE OF I.E. OR IMPREGNATION	SOLID DENOMINATION	CRYSTALLINITY (%)	S_{BET} (m^2g^{-1})	N° ACID SITES (meq g^{-1} Cat)	RELATIVE ACID STRENGTH
I.E.	40% NH_4^+	H(40)-NaY	100	726	1.2	STRONG
I.E.	64% NH_4^+	H(64)-NaY	100	713	1.8	STRONG
I.E.	0.5 wt % Pt	Pt(0.5)-NaY	100	680	0.1	WEAK
I.E.	40 NH_4^+; 2.0 wt % Pt	Pt(2.0)H(40)-NaY	100	638	1.2	STRONG
MOBIL METHOD*	-	ZSM-5	YES	351	1.6	STRONG
I.E.	1 wt % Co(as Co_3O_4)	Co(1)-NaY	100	722	0.16	MODERATE
IMPREGNATION	2 wt % Mo(as MoO_3)	Mo(2)-NaY	85	615	0.05	MODERATE
I.E.; IMPREG.	1 wt % Co(asCo_3O_4) 0.5 wt % Mo(asMoO_3)	Co(1)Mo(0.5)-NaY	90	710	0.20	MODERATE
I.E.	3.5 wt % Ni(asNiO)	Ni(3.5)-NaY	100	744	0.34	STRONG

* ZSM-5 catalyst was provided by Mobil Co.

I.E. = Ionic Exchange

TABLE 4. THERMOGRAVIMETRIC ANALYSIS FOR MIXTURES S/C = 1/1 (wt/wt)

CATALYST	HEATING RATE (DEGREE / MIN)	S = POLYISOPRENE				S = N-PARAFFINS				S = RESINS			
		T INF. (°C)	% W.L.INF.	T_F (°C)	% WL F	T.INF. (°C)	% W.L.inf.	T_F (°C)	%WL F	T_{INF} °C	% WL_{INF}	T_f	% W_f
-	20	390	42.9	460	82.9	370	64.0	430	95.4	350	46.1	450	82.1
ZSM-5	20	385	50.0	450	91.5	350	50.6	480	91.0	310	41.6	350	84.4
H(40)NaY	20	375	49.8	450	78.4	320	51.8	460	93.5	310	37.5	450	77.4
H(64)NaY	20	370	38.1	480	72.4	330	46.6	450	92.5	295	38.5	400	75.4
Pt(0.5)NaY	20	400	36.6	470	57.4	315	23.9	450	68.7	270	27.9	400	60.0
Co(1)NaY	20	350	31.5	450	91.9	310	39.1	450	89.7	300	36.9	450	75.0
Mo(2)NaY	20	350	29.2	450	71.9	325	38.5	450	98.2	320	48.4	450	98.4
Co(1)Mo(0.5)NaY	20	370	48.4	450	87.4	320	41.8	450	94.8	300	43.7	400	83.6
-	40	406	33.1	490	88.4	390	55.2	480	85.9	380	41.4	450	78.3
ZSM-5	40	390	42.8	500	96.1	360	46.2	480	84.4	350	44.8	460	80.5
H(40)NaY	40	390	47.3	470	88.6	-	-	-	-	330	40.9	420	81.8
H(64)NaY	40	370	40.3	480	80.8	350	45.4	470	94.6	310	40.2	400	82.4
Pt(C.5)NaY	40	340	25.3	500	75.0	330	24.5	460	61.8	300	34.8	450	77.0
Co(1)NaY	40	380	34.2	500	96.2	330	37.6	450	90.8	300	43.9	450	95.2
Mo(2)NaY	40	370	37.3	450	88.6	350	38.1	450	91.5	330	49.6	450	97.4
Co(1)Mo(0.5)NaY	40	385	48.1	450	89.8	340	37.8	490	88.3	330	38.9	450	87.3
-	80	425	51.1	510	93.3	420	53.0	490	82.9	430	38.5	510	92.0
ZSM-5	80	400	46.6	500	97.7	390	40.0	470	89.7	420	40.0	500	90.3
H(40)NaY	80	390	42.5	460	86.0	380	43.9	460	89.5	400	38.9	500	87.0
H(64)NaY	80	400	39.2	480	79.4	360	46.7	480	92.2	-	-	-	-
Mo(2)NaY	80	410	45.0	510	82.1	390	45.0	510	92.0	385	50.0	510	92.9
Co(1)Mo(0.5)NaY	80	400	49.1	510	89.6	380	44.6	500	87.9	420	36.0	520	89.4
Ni(3.5)NaY	80	360	38.8	500	74.8	370	29.0	510	85.4	350	41.1	520	96.0

T inf. = Temperature of inflection point.
% wl inf. = % of weight loss of sustrate At $T_{inf.}$
T_F = Temperature where weight loss finishes
% wl_f = % of weight loss of sustrate At T_f

TABLE 5

THERMOGRAVIMETRIC ANALYSIS FOR MIXTURES S/C = 7/3 (wt/wt)

CATALYST	HEATING RATE (DEGREE/MIN)	S = POLYISOPRENE				S = N-PARAFFINS				S = RESINS			
		T INF. (°C)	% W.L.INF.	T_F (°C)	% WL F	T.INF. (°C)	% W.L.inf.	T_F (°C)	%WL F	T_{INF} °C	% WL_{INF}	T_f	% W_f
-	20	390	42.9	460	82.4	370	64	430	95.4	350	46.1	450	82.1
ZSM-5	20	380	53.3	460	92.4	350	47.5	460	84.2	330	50.8	420	78.7
H(40)NaY	20	390	56.0	460	78.0	350	58.6	480	97.8	330	37.6	400	69.2
H(64)NaY	20	400	61.8	480	77.6	350	52.8	480	83.1	300	46.3	400	93.6
Pt(0.5)NaY	20	380	36.0	450	61.6	330	37.1	450	70.3	320	59.9	400	93.2
Co(1)NaY	20	350	29.9	500	91.2	350	50.8	450	91.2	320	40.6	450	87.3
Mo(2)NaY	20	360	40.2	450	84.3	350	65.4	450	93.2	330	49.9	450	96.5
Co(1)Mo(0.5)NaY	20	350	39.8	500	94.8	350	54.9	450	95.8	330	40.3	450	94.6
-	40	406	33.1	490	88.4	390	53.2	480	85.9	380	41.4	450	78.3
ZSM-5	40	400	60.2	460	93.2	350	41.6	480	83.9	350	50.4	390	73.8
H(40)NaY	40	400	49.3	470	78.2	360	61.7	460	95.2	350	49.2	400	67.7
H(64)NaY	40	400	52.7	480	80.1	350	46.0	480	78.2	330	48.0	450	88.3
Pt(0.5)NaY	40	400	40.2	400	72.9	390	35.8	450	60.0	330	39.6	400	75.1
Co(1)NaY	40	370	38.2	500	86.4	350	54.5	450	97.4	350	51.9	450	90.8
Mo(2)NaY	40	400	68.9	500	94.0	350	61.6	450	91.7	350	63.6	450	95.1
Co(1)Mo(0.5)NaY	40	380	46.0	450	93.9	350	46.9	450	91.2	350	63.3	500	97.4
-	80	425	-	510	93.3	420	53.0	490	82.9	430	38.5	510	92.0
ZSM-5	80	420	54.4	480	91.8	470	45.3	450	65.2	-	-	-	-
H(40)NaY	80	-	-	-	-	360	47.2	480	95.4	-	-	-	-
H(64)NaY	80	400	34.5	480	65.4	380	46.2	480	95.9	-	-	-	-
Mo(2)NaY	80	-	-	-	-	-	-	-	-	-	-	-	-
Co(1)Mo(0.5)NaY	80	-	-	-	-	-	-	-	-	-	-	-	-

T inf. = Temperature of inflection point.
% wl inf. = % of weight loss of sustrate At $T_{inf.}$
T_F = Temperature where weight loss finishes
% wl_f = % of weight loss of sustrate At T_f

Results for mixtures S/C = 1/1 wt/wt were more reproducible and consistent than results for mixtures S/C = 7/3 (wt/wt). Then the work continued only with mixtures S/C = 1/1 wt/wt, because for mixtures with lower contents of catalysts the effect of these on the pyrolysis could not be assured.

Regarding the effect of the heating rate, and according to the results of Table 4, as the heating rate increases, the T_{infl} and in most cases % WL final (i.e. conversion) also do it. Therefore in the catalytic pyrolysis of extracts from hydrocarbon producing plants high heating rates ($\geqslant$80°/min) should be utilized.

The T_{infl} was around 330 to 420°C and it was higher for the substrates without catalysts showing that the catalysts sped up the pyrolysis. The percents of weight loss at this point were from 37 to 64%. Therefore it could be assumed that most of the pyrolytic products are formed around 400°C and this temperature should be used in the future development of the pyrolytic technology.

Finally, the % WL f, and therefore the percent of conversion for all the sustrates, at a given S/C ratio and heating rate, were improved in most cases by using the synthesized catalysts.

c.- **DSC analysis**

Calorimetric studies were carried out on a DSC-system, upon heating from 30 to 500°C at 80°C/min. The samples were sealed in aluminium pans like in 4b and the volatiles, were flushed out of the reaction zone with a constant flow of N_2. The heats of pyrolysis ($\Delta H_{tot} = \Delta H_{endo} + \Delta H_{exo}$) were calculated as usual.

The calculated heats (ΔH_{tot}) were in the range of 17 to 199 cal/g but do not have physical significance. Since the volatiles are removed from the system, at T $\geqslant$ T inf (TG results), the mass of the system varies in a great extent and most of the sample is lost before reaching the final temperature. Thus the heats of pyrolysis can not be accurately determined from the peak area without correction, which would be specific for each case. On the other hand, the values of ΔH tot were small in comparison with the values of the ΔH combustion for the pyrolytic products of related mixtures S/C 1/1 wt/wt (Table 7). Therefore the ΔH tot. values are not determinative in in the selection of best catalysts and the DSC data has interest mainly from

a qualitative point of view.

In the DSC analysis, the pyrolysis of the mixtures S/C = 1:1 (wt/wt) could be separated into two large and broad peaks: one endothermic, with maxima around 200°C, the other, exothermic, with maxima around 430°C. Results for mixtures S/C = 1/1 (wt/wt) are given in Table 6.

TABLE 6

DSC ANALYSIS OF SUBSTRATES AND MIXTURES S/C = 1/1 wt/wt

Substrate	Peak endo Range temp.[a]	$T_{máx}$[b]	Peak exo Range temp.[a]	$T_{máx}$[b]
n-paraffins (Par)	77-437	357	437-497	
Par/ZSM-5*	87-372	-	372-497	417
Par/H(40)NaY	107-347	-	347-417	412
Par/Pt(0.5)NaY	87-397	187	397-442	407
Par/Co(1)NaY	97-397	177	397-497	427
Par/Mo(2)NaY	107-407	-	407-487	437
Par/Co(1)Mo(0.5)NaY	77-227	167	287-497	467
Poliisoprene (Pol)	97-357	-	357-497	427
Pol/ZSM-5	87-337	-	357-467	427
Pol/H(40)NaY	157-307	227	327-417	407
Pol/Pt(0.5)NaY	77-327	217	347-477	427
Pol/Co(1)NaY	77-157	117	157-197	177
	197-287	217		
	397-497	-		
Pol/Mo(2)NaY	77-147	117	147-187	177
	187-347	227	357-487	427
Pol/Co(1)Mo(0.5)NaY	77-277	227	277-467	-
	467-497	-		
Resines (Res)	227-377	207	377-497	477
Res/ZSM-5	107-347	-	367-497	457
Res/H(40)NaY	77-417	227	417-467	427
Res/Pt(0.5)NaY	97-397	227	-	-
	397-497	447		
Res/Co(1)NaY	157-297	227	362-497	-
Res/Mo(2)NaY	77-367	237	367-497	457
Res/Co(1)Mo(0.5)NaY	77-347	217	397-497	-

a.- Range of temperature of endo or exo peak

b.- Temp. of the maximun of the endo or exo peak. If a maximun was not appreciable is indicated by -.

Below 300°C a minimal amount of volatile material is generated (Table 4), and the first range endothermic peak is probably due to melting and minor scissions. On the other hand, the second range temperature, exothermic peak, is located, within the experimental error, in the zone of maxima volatization rate (Tables 4 and 6), therefore, an extensive decomposition seems to take place around 400°C, coinciding with T_{inf}.

The temperature of the maxima of the exotermic peak is lower for most of mixtures S/C than for the substrates without catalyst showing that they speed up the pyrolysis.

d.- Estimation of the heat of combustion of the pyrolytic products

The effect of 7 catalysts in the pyrolysis of the E.copiapina CH_2Cl_2 extract was studied by estimating the heat of combustion of the pyrolytic products of mixtures CH_2Cl_2 extract/catalyst = 1:1 (wt/wt). The ΔH_{comb} of the pyrolytic products could not be calculated by means of DSC due to equipment restrictions. An adiabatic calorimeter Parr 1108 was utilized under the following conditions: O_2 = 15 atm; time of combustion = 10 minutes, size of sample = 0.5 g. The results are given in Table 7.

The values of Δ H comb. in Table 7 may or not be identical to that of the pyrolytic mixtures obtained in the TG or DSC systems, because it is not possible to increase the temperature at constant rate in the adiabatic calorimeter as it can do it in the TG or DSC systems. Nevertheless, the estimated heats of combustion correspond to the products obtained by catalytic pyrolysis of the same sustrate with different catalysts under identical experimental conditions. Then they reflect the composition of the different pyrolytic mixtures, obtained under same conditions of time, temperature and O_2 pressure. Therefore it is possible to predict the relative capacity of the catalysts to produce mixtures with low C/H ratio.

Regarding the percentage of conversion (% WL f) and the heat of combustion, the best catalysts would be: ZSM-5, Mo(2) NaY and Co(1)Mo(0.5)NaY. On the other hand, and in concordance with previous results, the less effective catalyst would be Pt(0.5)NaY.

TABLE 7

TG ANALISIS, DSC ANALYSIS AND HEAT OF COMBUSTION OF E.COPIAPINA CH_2Cl_2 EXTRACT.

Catalyst	T_{inf} (°C)	% WL_{inf}	T_f (°C)	% WL_f	ΔH com pyrol.prod. (cal/g)	ΔH pyrol. (cal/g)
ZSM-5	360	58.0	510	79.4	7990	181
H(40)NaY	430	62.0	490	71.5	7280	202
Co(1)NaY	380	41.0	490	75.2	8150	180
Mo(2)NaY	405	49.5	510	83.5	8480	234
Co(1)Mo(0.5)NaY	350	52.0	490	69.5	8810	216
Pt(0.5)NaY	-	-	-	-	6840	194
Ni(3.5)NaY	348	64.0	520	75.2	8080	139

S/C = 1:1 (wt/wt)

S = CH_2Cl_2 Extract of E.copiapina

$T_{infl.}$ = temperature of inflection point

% $WL_{inf.}$ = % of weight loss of CH_2Cl_2 extract at $T_{inf.}$

T_f = temperature where weight loss finishes

% WL_f = % of weight loss of CH_2Cl_2 extract at T_f

ΔH comb.= heat of combustion in calories per gram of CH_2Cl_2 extract.

ΔH pyrol. = heat consumed during the pyrolysis per gram of CH_2Cl_2 extract.

5.- **Method of analysis of pyrolitic products.**

The combined TG- mass spectroscopic system developed by Pavlath and Gregorski was not available for the analysis of pyrolytic products. The mass spectrometer broke and could not be repaired. (WRRC, Albany, San Francisco September 1989). Therefore an alternative method of analysis was developed, utilizing TG and GC. ZSM-5, Mo(2)NaY and H(40)NaY were selected for these studies in order to compare the relative composition of the pyrolytic products with the previous results of ΔH comb. and the relative acid strenght of the catalysts.

a) **Determination of retention times of C_1 to C_7 hydrocarbons.**

A Hewlett Packard 5710A gas chromatograph with a Hewlett Packard 3390A integrator was utilized, under the conditions specified in Table 8. Gas standards from C_1 to C_7, which are the most probably volatile products, were utilized. 0.5 to 1.0 ml of each standard was injected with a 1 ml tight syringe.

TABLE 8

RETENTION TIMES OF SOLUTES IN HAYSEP-D

Solute	Retention time* (min)
C_1	
Methane	0.49 - 0.52
C_2	
Acetylene	1.34 - 1.38
Ethylene	1.42 - 1.45
Ethane	1.84 - 1.87
C_3	
Propylene	4.71 - 4.77
Propane	5.14 - 5.21
Propyne	5.27 - 5.31
C_4	
Isobutane	8.89 - 8.94
1,3-Butadiene	9.06 - 9.12
1-Butene	9.14 - 9.20
trans-2-Butene	9.47 - 9.57
Butane	9.67 - 9.72
C_5	
2,2-Dimethylpropane	12.02 -12.08
1-Pentene	13.41 -13.53
2-Methylbutane	13.47 -13.55
Isoprene	13.71 -13.90
Pentene	13.96 -14.03
Cyclopentene	14.08 -14.09
Cyclopentane	14.68 -14.70
C_6	
2,2-Dimethylbutane	16.53 -16.54
2-Methylpentane	17.22 -17.29
Methylcyclopentene	17.23 -17.24
Methylcyclopentane	17.23 -17.25
1-Hexene	17.32 -17.42
3-Methylpentane	17.46 -17.52
Hexane	17.75 -17.81
Benzene	17.80 -18.90
Cyclohexene	17.86
Cyclohexane	17.87 -17.88
C_7	
Methylcyclohexane	18.68 -18.70
Toluene	18.69 -18.90
Methylcyclohexene	18.71 -18.42

* Average of 3 to 6 runs

Conditions:

Gas Chromatograph Hewlett Packard 5710A with a Hewlett Packard 3390A integrator.
Column: 6' x 1/4" glass packed with Haysep D 100/120 mesh
Temperature: 80 to 290°C at 8°C/minute, hold at 290°C for minutes.
Injector: 200°C
Detector: 300°C, FID
Flow rate: 30 ml/minute He

Santards: 1.- Gas mixtures from Scott Speciality gases:

Mix 223: C_2 to C_6 α-olefins in He

Mix 219: C_1 to C_6 n-paraffins in He

Mix 8: cyclopentene, 1-methylcyclopentene, cyclohexene, 1-methylcyclohexene, in N_2

Mix 7: cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, in N_2

Mix 30: Acetylene, propyne, 1-butyne, 2-butyne, in N_2

Mix 2: isobutane, 2,2-dimethylpropane, 2-methylbutane, 2,2-dimethylbutane, 2-methylpentane, 3-methylpentane, in N_2

2.- Pure gases from Aldrich Chemical Co: ethylene; trans-2-butene; 1,3-butadiene.

3.- Spectroscopy grade chemicals from Merck: isoprene, benzene, toluene.

Three columns were tried: 6' x 1/8" stainless steel, packed with Chromosorb 107 80/100 mesh; 6' x 1/8" stainless steel, packed with Porapak SQ; 6' x 1/4" glass, packed with Hayesep D 100/120 mesh. The Hayesep D colum worked better giving good resolution for most of the components of the standards of C_1 to C_7 hydrocarbons. At least three determinations were carried out in each case. The retention times for C_1 to C_7 hydrocarbons, under the specified experimental conditions that gave the best results, are given in Table 8.

b) Collection of pyrolytic products.

Pyrolysis of sustrates and mixtures S/C = 1:1 (wt/wt) S = n-paraffins, polyisoprene, resins; C = ZSM-5; Mo(2)NaY; H(40)NaY were carried out in a TG under the conditions previously utilized (Table 4). A cool trap was mountted by connecting, with a tygon tube, an U glass tube (6 mm o.d., 300 mm lenght) inmersed in a Dewar with liquid N_2, at the oulet of the TG. In order to prevent the condensation of the products inside the TG, the temperature of the glass tube was maintained at 150°C during the pyrolysis by placing a heating tape, coated with silicone rubber, over the glass tube.

After finishing the pyrolysis, when the temperature of the TG oven was cooled up to 100°C, the tygon tube between the U tube and the TG outlet was cut and a septum was introduced at both ends of the U tube.

c) GC analysis of the gaseous products.

To ensure a homogeneous gas sample, the syringe needle was inserted through the septum while the sample was still frozen, then as the sample was unfreezing the syringe plunger was worked in and out at least four times. When the sample was unfrozen a 1 ml sample was removed for analysis and 0.5 to 1.0 ml was injected in the chromatograph. At least two determinations were carried out in each case, under the same conditions utilized for the analysis of the standards. The chromatograms were reproducible within the experimental error (accuracy of analysis ± 10%). Results are given in Table 9.

The 3 tested catalysts changed the distribution pattern of the pyrolytic products related to that of the sustrates without catalysts. Also, for all the sustrates the catalyst Mo(2)NaY seems to be the most promising. It shifted more efficiently the relative percentage of hydrocarbons towards C_6 and C_7 - C_{10},

TABLE 9

RELATIVE COMPOSITION OF HYDROCARBONS IN PYROLITIC VOLATILE PRODUCTS

Sustrate	Hydrocarbons (% relative)[a] C_1	C_2	C_3	C_4	C_5	C_6	C_7^+
n-paraffins (Par.)	-	2.8	2.2	5.9	10.8	15.8	61.1
Par/ZSM-5	-	0.3	5.7	10.5	8.6	13.0	62.0
Par/Mo(2)NaY	-	0.6	0.2	0.7	3.4	15.8	78.7
Par/H(40)NaY	-	0.5	1.4	4.1	8.1	19.4	66.4
Polyisoprene (Pol.)	-	1.8	1.5	1.5	18.6	9.97	66.2
Pol/ZSM-5	-	2.8	3.7	4.6	5.3	8.44	74.7
Pol/Mo(2)NaY	-	2.4	1.2	1.2	6.5	15.03	73.05
Pol/H(40)NaY	-	3.2	3.9	7.7	7.1	12.95	64.10
Resines (Res.)	-	1.6	2.0	1.6	7.4	16.8	70.2
Res/ZSM-5	-	0.5	0.8	4.8	17.6	12.8	63.2
Res/Mo(2)NaY	-	1.4	1.3	2.1	5.7	15.9	73.6
Res/H(40)NaY	-	2.9	4.1	6.5	6.9	11.9	67.2

a: Percentage of the sum of the peak areas of all compounds lying from R_t = 0.51 to R_t = 24.83. Average of 2 to 4 samples. Results do not contain corrections for sensitivity factors.

Conditions: Same as in Table 4. Sustrate/catalyst = 1/1 (wt/wt).

wich coincides with the conclusions obtained from TG and ΔH comb. data.

Comparison of the relative composition of pyrolytic products for S/C mixtures of a given sustrate with catalysts of the same crystalline geometry, i.e. S_1/Mo(2)NaY with S_1/H(40)NaY, showed the expected trend: higher percentage of $C_6 + C_7$, lower percentage of $C_1 + C_2$ and higher ΔH comb. for the catalysts with lower relative acid strenght (Tables 7,9 and 3).

6.- Thermochemical transformations of whole extracts or latex

The suitability of the previously selected catalysts was tested by carrying out TG analysis of mixtures S/C = 1/1 wt/wt, where S = whole extract or latex from promising species of chilean arid lands.

The preparation of the samples S/C and the TG analysis were done as in 4a and 4b. Results are given in Table 10 and showed that the selected catalysts, under the

conditions of the work, could pyrolyze the extracts and latex with similar or even better efficiency than ZSM-5.

For all the sustrates without catalysts the % WL f was higher, in opposition with the previous results for the isolated components of the extracts or latex (Table 4), showing that the presence of other components (may be inorganic or polar organic compounds) affect the performance of the catalysts. Newertheless, according the results of Table 7, even the conversions were lower, the Δ H comb, and then the quality of the products as fuels were higher for the catalytic pyrolysis.

TABLE 10

TG ANALYSIS OF WHOLE EXTRACTS AND LATEX OF PROMISING SPECIES WITH SELECTED CATALYSTS

CATALYST	S = E. lactiflua latex				T. absinthioides CH_2Cl_2 extract				E.copiapina CH_2Cl_2 extract			
	T_{inf} (°C)	% W.L. inf.	T_f (°C)	% WL_f	T_{inf}	% W.L. inf.	T_f	% WL_f	T_{inf} (°C)	% WL_{inf}	T_f (°C)	% WL_f
-	405	65.4	505	90.7	418	47.9	530	79.4	420	65.4	511	92.5
ZSM-5	375	26.74	510	57.9	410	49.6	520	73.4	360	58.0	510	76.4
Mo(2)NaY	365	29.72	517	65.6	410	40.4	510	62.9	405	49.5	522	85.6
Co(1)Mo(0.5)NaY	390	40.3	527	74.8	415	32.0	535	63.7	350	52.0	490	71.9

T_{inf} = Temperature of inflection point

% WL_{inf} = % of weight loss of sustrate at T_{inf}

T_F = Temperature where weight loss finishes

% wl_f = % of weight loss of sustrate At T_f

IV. IMPACT, RELEVANCE AND TECHNOLOGY TRANSFER

a.- In this project we have established that the main components of the low polarity extracts, from different hydrocarbon producing plants, can be efficiently converted to chemicals and high grade fuels through pyrolysis, utilizing zeolitic faujasites catalysts. Our studies developed catalysts which were at least similar to, but generally more efficient that ZSM-5, the commercial catalyst designed Mobil Co. These basic studies were carried out in a thermoanalyzer at the miligram level. The results enable us to take the next step: a study at laboratory scale, preferably in a continuous reactor coupled with appropriate instrumentation.

b.- The project also brought about the establishment of a multidisciplinary research group of scientists from Chile and USA, that will continue working in other projects in the future.

c.- During the development of the project, high level scientists with capacity for contributing to the scientifical and technological development in Latin American countries were formed. Part of the work was carried out by graduate students from Ph.D. Programs at the University of Concepción.

d.- The principal investigator, invited by the BOSTID, could attend in Pakistan to a workshop with other AID grantees, working in the same field of research, with whom scientific exchange continues and possibility of future cooperative work is opened.

During the presentation of a paper at the 201st ACS Meeting she also could contact american scientists, working for Solar Energy Research Institute (SERI), with whom a proffesional relationship began and possibly joint research in the future would be achieved.

e.- The equipment provided under the grant, allowed to set up of a modern Thermal Analysis laboratory at the Chemistry Department, U. of Concepción, that will be utilized in the future by ours and other research groups.

V.- PROJECT ACTIVITIES/OUTPUTS

1.- Papers presented at Scientific Meetings:

- Análisis químico de n-alcanos y fracción de aceites de Euphorbia copiapina
  M.Montecinos, S.Gnecco.
  XVIII Jornadas Chilenas de Química, Santiago. December 1989.

- "Utilization of hydrocarbon producing plants native in arid areas: highlights"

S.Gnecco
PSTC Grantees Workshop & Int. Symposium of Biotechnology for Energy, Faisalabad, Pakistan, Dec. 1989.

- "Potencial de especies vegetales de zonas áridas como recurso energético para Chile"
S.Gnecco.
I Congreso Nacional de Energía: Chile, Santiago; April 1990.

- "Pyrolysis of Euphorbia copiapina dichlorometane extract with zeolitic catalysts"
S.Gnecco, M.Montecinos, R.Cid, R.Catalán.
XIII Reunión Soc. Brasileira de Química, Caxambú, Minas Gerais, Brazil, May 1990

- "Catalytic pyrolysis of n-paraffins and resins from CH_2Cl_2 extracts of hydrocarbon producing plants"
S.Gnecco, R.Cid. V.Caamaño, M.Parra, R.Catalán, M.Montecinos, A.Pavlath
XIX Congreso Latinoamericano de Química, Buenos Aires, Argentina, Nov. 1990.

- "Pyrolysis of natural rubber, waxes and resins with zeolitic catalysts"
S.Gnecco, R.Cid, V.Caamaño, A.Pavlath
201st ACS Meeting. Fuel Division. Atlanta, USA, April 1991.

2.- Training

- Part of the work of this project was carried out by graduates students at the Chemistry Department, U. of Concepción as a part of theirs Ph.D. thesis.

- During her stay at the Western Regional Research Center in 1989 and 1990, Dr. Gnecco got expertise in G.C. analysis of pyrolytic product and thermoanalysis (TG and DSC).

3.- Publications

Two papers: "Chemical analysis of n-alkanes and oil fractions from Euphorbia copiapina" and "Pyrolysis of E.copiapina CH_2Cl_2 extract with zeolitic catalysts" are being finished for submission within this year to Economy Botany and Applied catalysis. Also during next semester we would finish and submit,probably to Applied catalysis,at least one additional paper dealing with the work done under this grant. Publications will be sent to AID and to BOSTID as soon as they will be accepted.

VI. PROJECT PRODUCTIVITY

During the execution of the project we had problems which brought about the change of the estimated completion date and some methods of analysis proposed originally:

- Damage of the old TG equipment (discontinuation of repairs) and delay in obtaining the official approval and funds for the purchase of a new equipment, caused the change of the estimated completion date.
- Non availability of the TG-mass spectra computarized system at the WRRC, due to fortuitous break of the mass spectrometer, caused the change of the proposed method for analyzing the pyrolytic products by an alternative TG followed by GC method of analysis.

However, and regardless these changes, the project accomplished all the proposed objectives, on the contrary the scope of the research was increased. The extension of the period of the grant gave us the time to synthesize, characterize and try four catalysts, not included in the original proposal.

In summary:

- We have shown that the main components of extracts from hydrocarbon producing plants can be converted to chemicals and high grade fuels through pyrolytic reactions,using faujasites as catalysts.
- We established the best temperature and heating rate for the pyrolysis,on the basis of the TG and DSC results.
- We selected the more promising catalysts on the basis of results on TG composition of pyrolytic volatile products and ΔH comb.
- In our studies we synthesized, characterized and tested catalysts which were similar to, and in some cases more efficient than ZSM-5, the catalyst designed by Mobil Co.
- We established a multidisciplinary group of experts from U.S.A. and Chile that will continue working together in other research projects.

VII. FUTURE WORK

The results obtained at the miligram level enable us to take the next step: a atudy at laboratory scale, preferably in a continuous reactor coupled with appropiate instrumentation. Using the preselected catalysts and reaction conditions as starting points, the effect of various parameters will be determined. The parameters to be investigated will include among others: pressure, contact of substrate with catalysts, metal content (Co or Mo) in the catalysts, deactivation, presence of H_2 in the system. Some of the investigators will continue work in the next years in collaboration with the Research Group on Catalysis at the University of Santiago, and most likely with a research group of the Solar Energy Institute in Golden, Colorado.

Before establishing the "energy crops" it will be necessary to improve the yield of hydrocarbon in the selected species and to find out suitable methods for the mass propagation. Both subjects would be undertaken in other research project.

VIII REFERENCES

1.- M.Calvin, Science, 219, 24 (1983)

2.- C.Kirsche, P.Viaud, Entropie, 17, (98), 32 (1981)

a. B.N. Timmermann, and J.J. Hofman, in Plants for arid lands, G.E. Wickens y al. eds. George Allen & Unwin, London, 1985, pp. 337-368.

b. D.O. Hall, ibid, pp. 369-384

c. R.J. Newton, J.R.Goodin, ibid, pp. 385-397

3.- M.O. Bagby, R.A. Buchanan, F.H. Otey, in ACS Symposium Series, N°144, D.L. Klass, ed. ACS, 1981, pp. 125-136.

4.- M.E.Carr, B.S. Phillips, M.O.Bagby, JACCS 62 (a) 1367 (1985)

5.- J.R. Benemann, en The Biosaline Concept. A.Hollaender ed., Plenum Press, New York, 1979, pp. 309-331.

6.- S.Gnecco, J.Bartulín, C.Marticorena, A. Ramírez. Biomass 15, 165- (1988).

7.- S.Gnecco, J.Bartulín, C.Marticorena, J.Becerra, Phytochemistry, 28 (4) 1254- (1989).

8.- S.Gnecco, J.Bartulín, A.Ramírez. Química & Industria, 1 (2), 34 (1989).

9.- J.N. Miale, N.Y. Cher, P.B. Weisz, J.Catal., 6, 278 (1966).

10.- P.W. Weisz, W.O. Haag and P.G. Rodewald, Science, 206, 57 (1979).

11.- J.Diebold, J.Scahill in Pyrolysis oils from Biomass, Producing, Analizing and Upgrading. E.J. Soltes, T.A. Milne Eds, ACS, 1988, pp 264-276.

12.- Y.S. Prasad , N. Bakhshi, J.F. Mathews, R.L. Eager, The canadian Journal of Chem. Eng. 64, 278 (1986).

13.- R.Cid, R.Arriagada, F,Orellana. J.Catal. 80, 228- (1983).

14.- R.Cid, R.Arriagada, F.Orellana. Bol.Soc.Chil.Quím. 30(2), 63(1985)

15.- R.Cid, F.Orellana and A. López-Agudo. Applied Catalysis 32, 327 (1987)

16.- R.Cid, G.Pecchi, Applied Catalysis, 14, 15 (1985).