

Biofuels from catalytic cracking of tropical vegetable oils(1)

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Abstract. — Once the local food market has been supplied, vegetable oils could be available as fuels in isolated areas such as islands and especially in developing countries where favorable situations can be found. Among the various uses of vegetable oils as fuels the catalytic cracking is one of the most versatile, especially for solid fats. The two steps (cracking and distillation) that were checked, yielded 85 % of the initial energy content of the starting oil as gaseous and liquid hydrocarbons. The gasoline and the diesel fuel fractions which account for 50 w% of the substrate have an interesting hydrocarbon composition close to fossil fuels'. The process energy would require only a part of the evolved gases. The catalytic cracking of tropical vegetable oils is therefore an attractive opportunity to add on-site value to low price agroproducts and to help the economic development of rural areas.

Key words. — Vegetable oils, catalytic cracking, hydrocarbons, fuels, bioenergy

INTRODUCTION

Vegetable oils could be available as fuels in some regions without affecting nutritional needs. This is particularly the case for isolated areas - small islands and places away from ports and factories - and especially in developing countries where different situations can be found: (i) unharvested oilseeds, (ii) local overproduction, (iii) low international prices of agroproducts, (iv) high transportation fares of crude agroproducts, (v) high prices of fossil fuels. The direct use of oils would be the simplest way indeed but it may cause troubles in diesel engines. It is then necessary to convert oils into methyl or ethyl esters; however, the availability of methyl and ethyl alcohols is the main drawback. Moreover, these esters do not work with gasoline engines.

Results on pyrolysis and catalytic cracking of biomass, including vegetable oils, have been reported elsewhere (Arida *et al.*, 1986; Churin *et al.*, 1989; Dos Anjos *et al.*, 1983; Graille *et al.*, 1981; Milne *et al.*, 1990; Weisz *et al.*, 1979). We therefore investigated the cracking of vegetable oils: we see it as an interesting alternative in developing countries for those where the excess of harvested biomass could be used as an energy source.

MATERIALS AND METHODS

Copra oil and palm oil stearine are commercial grade refined, bleached, deodorized products. The laboratory micro-pilot plant used for these runs and many of the analytic procedures have been described in a previous paper (Graille *et al.*, 1981). Analysis of the cracking gases by GC (Carlo Erba 2450): column Porapak Q 50/80 mesh, length 6 m, ID 4,6 mm; oven 40 °C 3 min, 40-240 °C at 30 °C/min, 240 °C, 20 min; injection 3 ml, 200 °C; detector, catharometer, intensity 100 mA, 200 °C; carrier gas: helium 50 ml/min. Analysis of the COP (condensed organic phase) by HPLC (Spectra Physics SP 8700): column I NH₂/CN Partisil (Whatman) length 25 cm, ID 4,6 mm, particle diameter 5 µm; column II

Microporasil (Whatman) length 25 cm, ID 4,6 mm, particle diameter 10 µm; solvent n-hexane (HPLC grade, Carlo Erba) flow rate 1 ml/min, 8,4 min; 1,5 ml/min, 19.6 min; 3 ml/min, 15 min; backflush at 28 min; injection volume 10 µl; detector, differential refractometer R401 (Waters). Analysis of the COP by GC/MS (Carlo Erba 2450/LKB mass spectrometer): column OV1, length 126 m, ID 0,28 mm, film thickness 0,3 µm; oven 50 °C, 8 min; 50-230 °C at 5 °C/min; 230-330 °C at 10 °C/min; 330 °C, 10 min; injector split ratio 1/60, 250 °C; detector FID 275 °C or mass spectrometer IP 70 eV, 250 °C.

TABLE I. — Fatty acid compositions and physical properties of copra oil and palm stearine

Fatty acids (w%)		Copra	Palm stearine
Caproic	C 6:0	1.2	—
Caprylic	C 8:0	8.5	—
Capric	C10:0	6.4	—
Lauric	C12:0	48.3	0.1
Myristic	C14:0	17.8	1.3
Palmitic	C16:0	8.9	55.1
Stearic	C18:0	2.5	4.3
Oleic	C18:1	5.3	31.9
Linoleic	C18:2	1.1	7.1
Linolenic	C18:3	—	0.2
Acidity (w%)		0.2	0.7
Iodine value		8	39
Melting (°C)		21-23	40-45

RESULTS AND DISCUSSION

Since the beginning of our work in that field (Graille *et al.*, 1981; Stern *et al.*, 1983), we have been testing several oils and derived free fatty acids, either from tropical (palm, copra, tung) or tempered (rape and linseed) crops covering a wide range of unsaturation and chain length patterns. We report here the main results concerning the cracking of two tropical vegetable oils, palm oil solid fraction (stearine) and copra oil, over a standard petroleum FCC catalyst SiO₂/Al₂O₃, 87/13, at 450 °C as described previously.

The fatty acid composition of the two refined oils that had been chosen are given in table I. Copra oil, which is extracted from the dried albumen of coconuts, contains mainly lauric (C12:0) and myristic (C14:0) acids; palm stearine coming from the cold fractionated crystallization of the oil extracted

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from the pulp of oil palm fruit contains mainly palmitic (C16:0) and oleic (C18:1) acids. These oils melt at a temperature higher than 20 °C due to their high content of saturated fatty acid.

Catalytic cracking products and byproducts

The catalytic cracking of vegetable oils, which is nothing more than the reduction of the molecular weight, gives several type of products, either gaseous, solid or liquid. There are two liquid phases condensed at room temperature (Fig. 1).

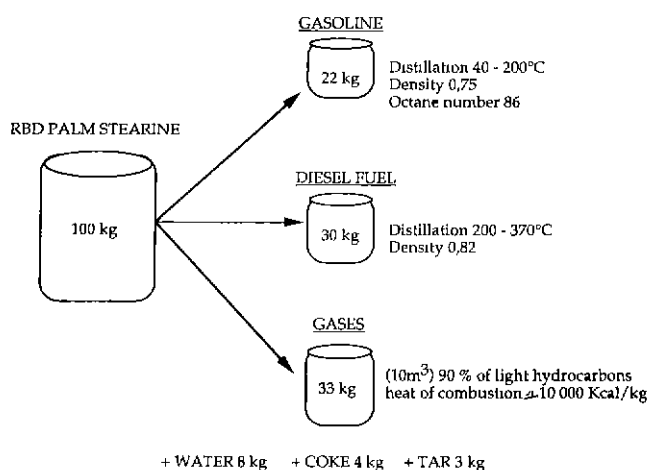


FIG. 1. — Catalytic cracking of palm stearine

The main liquid fraction is an organic phase accounting for 53-55 w% of the starting oil. The low acidity level of this COP (condensed organic phase) and the fact that there are no IR stretching bands of glycerides at 1725 cm⁻¹ (C=O), nor 1150-1200 cm⁻¹ (C-O-C) show that the thermocatalytic process has already transformed quite all the carboxylic groups. Thus, the COP contains more than 96 w% of hydrocarbons. Besides the COP, the condensate also contains an aqueous phase of about 8 w% of the starting oil. The formation of water cannot be avoided in this process, owing to the presence of the oxygen atoms of the ester group accounting of 13.5 and 11.2 w% of the substrates, copra and palm stearine respectively. The water phase separates easily in the condenser. The remaining oxygen is found in the gaseous products, mainly as carbon monoxide and carbon dioxide and also as water vapor. However, the cracking gases which account for 33-35 w% of the substrate have a high hydrocarbon content: 74 w% for copra and up to 84 w% for palm stearine.

The deposit of coke as a byproduct (about 4 w% of the starting oil) on the catalyst surface cannot be avoided during the catalytic process, especially for the amorphous aluminosilicates group to which pertains the low cost catalyst chosen for these runs. The decreasing cracking activity of the catalyst due to the coke formation is fully restored by burning out at 550 °C for 2 hours, with an air stream.

The fuels

Virtually, all the cracking products, except carbon dioxide and water, can provide energy by combustion. For example, the heat produced during the catalyst regeneration step can be used for the heating of a second reactor or the distillation unit. The cracking gases, which contain more than 70 w% of light hydrocarbons, have an estimated heating value ranging from 32000 to 33500 KJ/kg for copra and palm stearine respectively. They could be used as an energy source for the

plant. The 90 % v/v distillation temperatures of the COP are 250 °C and 302 °C for copra and palm stearine respectively. The COP was fractionated by distillation to obtain biogasoline and biodiesel fuel as for fossil fuels. Concerning the gasoline fractions, as shown in table II, their properties are close to those of the fossil fuels: the biogasolines are richer in heavy hydrocarbons simply because we collected this fraction up to 200 °C in order to increase the yield.

TABLE II. — Physical properties and chemical composition of bio and fossil fuels

	Copra	Palm stearine	Fossil fuel
	Gasoline		
Yield (w% starting oil)	30	22	—
Density	0.74	0.75	0.75
Octane Number	91	86	90 ⁽¹⁾
Distillation °C			
10%	55	59	53
90%	182	187	170
Hydrocarbon composition			
Saturated	46	38	15
Olefins	36	27	34
Aromatics	18	35	51
	Diesel fuel		
Yield (w% starting oil)	21	29	—
Density	0.82	0.82	0.84
Distillation °C			
10%	207	214	204
90%	217	288	351
Hydrocarbon composition			
Saturated	75	65	67
Olefins	0	0	0
Aromatics	25	35	33

(1) hydrocarbons alone, without additives

The chemical compositions have been investigated either by liquid chromatography to separate the main fractions -saturated, olefins, aromatics- and by gas chromatography coupled to mass spectrometry to identify as many hydrocarbons as possible. These results show that the biogasoline content of aromatics is substantially lower than that of fossil gasoline, especially for palm derivatives; the olefins content that has to be minimized is in the same range. Fortunately, the saturated hydrocarbons of the main fraction have a high content of branched chains, thus leading to a fairly high research octane number for this one-step process, in spite of the low aromatic content.

Concerning the diesel fractions, the chemical compositions are close to the fossil fuels'; the density of the biofuels, somewhat lower than that of the fossil fuel is in accordance with its much higher 90 % distillation temperature due to the presence of heavy hydrocarbons coming from the crude petroleum. One has to point out that these fractions, with (i) a high content of normal paraffins, (ii) no olefins and no heavy hydrocarbons, could have interesting properties as diesel fuels.

Energetic yield

The energetic self-sufficiency of the palm oil crop has been already discussed in previous papers (Graille *et al.*, 1981; Stern *et al.*, 1983). We only report here the energy balance for the production of biofuels by catalytic cracking and distillation. Assuming that the coke (= 4 w%) and the

distillation residue (tar = 3 w%) are not used as energy source, and using data from fossil hydrocarbons refining, the calculation shows that the processing of one metric ton of vegetable oil (37000 KJ/kg) yields 34500 MJ as liquid and gaseous fuels, while the energy consumption would be 3000 MJ. The energy necessary for the process could come either from the lignocellulosic harvested biomass (Graille *et al.*, 1981; Stern *et al.*, 1983) or from the cracking gases. In this last case, more than the two third of the cracking gases would still remain available (250 kg) along with gasoline and diesel fuel (520 kg). Thus, from an energetic point of view, the yield is close to 85 %.

CONCLUSION

Among the various uses of vegetable oils as fuels, catalytic cracking is one of the most versatile, especially for solid fats. This simple, two-steps process, yields gasoline whereas transesterification with methanol or ethanol only gives diesel fuel. There is no waste water effluent nor air pollution and the short cycle carbon dioxide, rejected either by the plant itself or by the engines run with biofuels, does not contribute to the greenhouse effect. For all these reasons, the catalytic cracking of tropical vegetable oils is an attractive alternative to add on-site value to low price agroproducts and to help economic development of rural areas. At this stage, it would be necessary to carry out pilote-scale experiments to assess the economic parameters and also to obtain large samples of biofuels for long term engine tests.

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RESUME

Synthèse de biocarburants par craquage catalytique d'huiles végétales d'origine tropicale

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Après satisfaction du marché alimentaire local, les huiles végétales pourraient trouver un débouché comme carburant dans les régions isolées qui présentent des situations favorables, tels les îles et les pays en développement. Le craquage catalytique est l'une des plus intéressantes formes d'utilisation des huiles à des fins énergétiques, en particulier pour les produits concrets. Le procédé en deux étapes étudié (craquage et fractionnement par distillation) conduit à des hydrocarbures (gazeux ou liquides) représentant 85 % de l'énergie initialement disponible dans l'huile. Les fractions liquides, essence et gazole, soit 50 %p du substrat de départ, ont une composition voisine de celles des carburants pétroliers. De plus, une partie seulement des gaz de craquage suffit à fournir l'énergie nécessaire au procédé. Le craquage catalytique des huiles végétales tropicales constitue donc une alternative intéressante pour valoriser localement les productions agricoles de faible valeur marchande et aider ainsi le développement économique des régions productrices.

Mots clés. — Huiles végétales, craquage catalytique, hydrocarbures, carburants, bioénergie.

RESUMEN

Síntesis de biocarburantes por cracking catalítico de aceites vegetales de origen tropical

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Después de haber atendido el mercado alimenticio local, los aceites vegetales podrán encontrar una salida como carburante en las regiones aisladas que presentan situaciones favorables, tales como las islas y los países en vías de desarrollo. El cracking catalítico es una de las más interesantes formas de utilización de aceites para fines energéticos, especialmente para productos concretos. El procedimiento en dos etapas estudiado (cracking y fraccionamiento mediante destilación) desemboca en hidrocarburos (gaseosos y líquidos) que representan el 85 % de la energía inicialmente disponible en el aceite. Las fracciones líquidas, esencia y gasoil, o sea el 50 % del sustrato inicial, tienen una composición parecida a la de los carburantes petroléos. Además, tan sólo una parte de los gases de cracking basta para proporcionar la energía precisa al procedimiento. El cracking catalítico de los aceites vegetales tropicales constituye pues una alternativa interesante para valorizar las producciones locales agrícolas de bajo valor mercantil y ayudar así al desarrollo económico de las regiones productoras.

Palabras claves. — aceites vegetales, cracking catalítico, hidrocarburos, carburantes, Bioenergía.

