

TITLEProduction of Synthetic Crude Petroleum

This invention is concerned with the conversion of plant oils and animal oils and other substances derived from them and natural and processed rubbers such as vehicle tyres and tubes into hydrocarbons and chemicals. More particularly, by the process of this invention, the above named substances are catalytically converted in an energy efficient high yield operation into hydrocarbons that are useful for the production of gasoline, kerosene, diesel and other chemicals. Further, this invention provides a process for producing hydrocarbons from renewable energy sources.

In recent years much work has centered on the use of vegetable seed oils and their derivatives, alone or in admixture with diesel, alcohol or gas oil, as diesel fuel in compression ignition engines. Results showed that such engines could run satisfactorily for short periods of time although prolonged operation with such fuels have revealed many problems ranging from engine wear, incomplete combustion, coking of nozzles and formation of polymeric material in the engine crank case.

There have also been prior attempts to produce synthetic fuels from other sources. Some examples of such fuel production are: recovery of syncrude from shale by in situ extraction with heated air and retorting; extraction of heavy oil from tar sands by heating with water and alkali and subsequent refining of the oil; Lurgi gasification of coal to syn gas; Fischer-Tropsch coal conversion into liquid syncrude; Mobil's gasoline from coal process; and anaerobic digestion of biomass to methane. However, these processes, besides being expensive, suffer from many disadvantages, chief of which are environmental pollution and disposal problems, undesirable low value by-products, and product streams that require multi-steps handling.

While olefins can be manufactured from carboxylic acids and esters by catalytic conversion with nickel catalysts containing tin, germanium or lead, the process is confined mostly to starting materials derived from saturated oils. For the process to be useful, the oils must first be subjected to a process of hydrogenation and then conversion to the acids or esters before the derived materials can be used in the process. Moreover, economic consideration is an important factor because of the many steps involved and the need for further processing before the final products can be used as

fuels.

Catalytic conversion of biomass into fuels involving aluminosilicate zeolites have also been reported. However, this method suffers from the disadvantages of low yields, extensive coke formation and rapid poisoning of the catalyst.

As the 21st century and possibly the twilight of the fossil fuel era approaches, the availability of alternative fuel supplies continues to be of major global concern. Increasing cost of petroleum, a major source of fossil energy, is inevitable because of limited availability. As plant oils and animal oils and rubbers are renewable energy sources, the ability to convert them into hydrocarbon fuels in a simple straightforward energy efficient process would certainly add a new dimension in the quest for a solution to the global energy problem.

It has now been discovered that biomass materials such as plant oils and animal oils, including fatty acids, esters and related substances derived from them and natural and processed rubbers such as vehicle tyres and tubes, can be converted directly in a simple energy efficient catalytic process to hydrocarbons in high yields.

According to this invention there is provided a process for producing synthetic crude petroleum by

catalytically cracking a biomass material (P) comprising (a) a plant oil or a product obtained therefrom and/or (b) an animal oil or a product obtained therefrom and/or (c) a rubber using a catalyst comprising alumina with or without silica but excluding any zeolite content, the total amount of silica, if present, constituting a lesser amount by weight, preferably no more than 25% by weight, of the catalyst mixture. The catalyst used may be substantially wholly alumina. The process may be carried out in the presence of a carrier gas, preferably a carrier gas comprising air or nitrogen or argon or helium or hydrogen or a hydrocarbon obtained from petroleum refining and cracking operations, e.g. methane.

The biomass material (P) may comprise triglycerides, fatty acids, esters and related substances derived from them. The rubber may be in the form of a vehicle tyre or tube.

It is a preferred feature of this invention that the said oils defined by (a) and (b) (which may be triglycerides of fatty acids wherein the fatty acid moiety ranges from 4 to 30 carbon atoms, the fatty acids most commonly being saturated or containing 1, 2 or 3 double bonds) need not be in anhydrous or pure form or be

subjected to prior hydrogenation by methods known in the art. The said oils may contain variable amounts of free fatty acids and/or esters both of which may also be converted to hydrocarbons during the process of this invention. As the said oils may be composed not only of natural glycerides but other materials like carotenoids, hydrocarbons, phosphatides, simple fatty acids and their esters, terpenes, sterols, fatty alcohols, tocopherols, polyisoprene, carbohydrates and proteins, for the purpose of this invention the said oils may contain such materials as part of their composition. It should be noted that in the case of the plant oils the preferred oils are palm oil, coconut oil, corn oil, soya oil, safflower oil, sunflower oil, linseed oil, olive oil and peanut oil. In the case of animal oils, the preferred oils are pork lard, beef fat, mutton fat and chicken fat. It is to be understood that for the purpose of this invention, mixtures of the oils, although of different origins, are suitable as feed to the catalytic conversion step. Thus mixtures of the plant oils, mixtures of the animal oils, and mixtures which include plant oils and animal oils are within the scope of this invention. Natural fatty acids and esters, other than triglycerides, also may be used in the process of this invention. Palm fatty acids and methyl esters derived

from transesterification of plant oils and animal oils, the residue and light ends fractions obtained during acid splitting of palm oil may be used. In the case of the said rubbers, the preferred rubbers are natural rubbers and processed rubbers such as vehicle tyres and tubes.

The catalyst useful in this invention comprises alumina with or without silica. For the purpose of this invention the preferred catalysts are Fluka Type 504C Alumina (pH 4.5), Fluka Type 507C Alumina (pH 7), Fluka Type 5016A Alumina (pH 9.5) and Merck Silica Gel 100 (70-230 mesh). Contacting the said oil or rubber or mixture thereof with the catalyst in the process of this invention may be carried out with the catalyst as a fixed bed reactor. Considered as within the scope of this invention, the catalyst can be used as a moving bed reactor, operated in a transport fashion such that the catalyst is cycled between a reaction zone and a regeneration zone, as is currently the practice in the petrochemical industry. It is to be noted that the contacting step can be conducted directly or in an atmosphere containing a gaseous substance such as air or nitrogen or argon or helium or hydrogen or other

hydrocarbons obtained from petroleum refining and cracking operations, for example methane; a preferred flow rate of the gas is from 30 ml/min to 1900 ml/min, a more preferred flow rate being 90 ml/min to 300 ml/min. After the contacting step the catalyst may be regenerated by heating in a stream of oxygen enriched air at a temperature from 550°C to 750°C. During the process of this invention, the pressure applied is preferably about 1 atmosphere to 10 atmospheres. A pressure of about one atmosphere will usually be satisfactory. The reaction temperature of the catalyst is preferably in a range from 300°C to 680°C, a more preferred reaction temperature being in a range from 420°C to 550°C. A preferred ratio of the catalyst weight to the oil or rubber weight is in a range from 1:1 to 10:1. For a fixed bed reactor, a more preferred value for every 2 to 6 parts by weight of the catalyst, one part by weight of the oil or rubber is fed per hour to the catalyst. Under the conditions of the catalytic reaction given above, gaseous and liquid hydrocarbons, coke, water and hydrogen sulphide may be formed. When rubber is used as feed stock, in addition to the products mentioned above, ammonia may also be formed. As described herein above, the hydrocarbons produced may be fractionally distilled to fractions suitable for the production of

gasoline, kerosene, diesel and other chemicals.

This invention will be illustrated by the following examples. They are given only to illustrate this invention and are not intended to limit the scope of the present invention.

Example 1

In this example, the results of which are shown in Tables 1 and 2, 160g of crude palm oil (free fatty acid content 3.5%), heated to a temperature of 120°C, was passed at a steady rate during 4 hr. over a fixed bed of 112g Fluka Type 504C alumina (pH 4.5) maintained at 510°C and one atmosphere pressure with nitrogen gas flowing at 120 ml per minute. The products were collected in three traps connected in series and cooled respectively in air, cold water and acetone-dry ice. The products in the traps were combined and after separation from the water, the oil was found to comprise hydrocarbons with no uncracked starting material.

Example 2

In this example, the cracking of 160g of palm fatty acids was performed with argon as the reagent gas under the same conditions as stated in Example 1. After separation from the water, the oil was found to comprise hydrocarbons without any uncracked starting material. The results are shown in Table 3.

Example 3

In this example the cracking of 160g of a mixture consisting of equal proportions of palm oil, coconut oil, corn oil, soya oil, safflower oil, sunflower oil, linseed oil, olive oil, peanut oil, palm fatty acids, pork lard, beef fat, mutton fat and chicken fat was performed as described in Example 1. After separation from the water, the oil was found to comprise hydrocarbons without any uncracked starting material. The results are shown in Table 3.

Example 4

In this example, the cracking of 160g of palm oil (free fatty acid content 3.5%) was performed with nitrogen as the reagent gas and a catalyst mixture containing 100.8g Fluka Type 504C Alumina (pH 4.5) and 11.2g Merck Silica Gel 100 (70-230 mesh) as described in Example 1. After separation from the water, the oil was found to comprise hydrocarbons without any uncracked starting material. The results are shown in Table 3.

Example 5

In this example, 160g of crude palm oil (free fatty acid content 3.5%) heated to a temperature of 120°C was passed at a steady rate during 4 hr. over a fixed bed of 112g Fluka Type 504C Alumina (pH 4.5) maintained at 510°. The products were collected as described in Example 1.

After separation from the water, the oil was found to comprise hydrocarbons. The results are shown in Table 3.

Example 6

In this example, the results of which are shown in Table 3, 49g of molten commercial hevea rubber (obtained previously by coagulating the rubber latex with formic acid, pressed between rollers to remove the liquid, then air dried and smoked) was passed at a steady rate during 1 hr. over a fixed bed of 112g Fluka Type 504C Alumina (pH 4.5) maintained at 510°C and one atmosphere pressure with argon as reagent gas as described in Example 1. After separation from the water, the oil was found to comprise hydrocarbons.

Example 7

In this example, the results of which are shown in Table 3, 40g of a used car rubber tube was placed in a glass tube and the temperature quickly raised to 510°C within about 20 minutes with argon flowing at 120 ml per minute. The molten rubber was then passed over a fixed bed of 78g of Fluka Type 504C Alumina (pH 4.5) maintained at 510°C and one atmosphere pressure during 35 minutes. After separation from the water, the oil was found to comprise hydrocarbons.

The various named catalysts like Fluka Alumina and Merck Silica Gel are commercially available materials.

"Fluka" Alumina Al_2O_3

"Merck" Silica Gel SiO_2

"Fluka" and "Merck" are registered Trade Marks.

TABLE 1 YIELD OF LIQUID HYDROCARBONS FROM CRACKING OF OILS

OIL	PO	CNO	CO	SO	SAO	SNO	LO	CO	PNO	PL	BF	MF	CF	PFA	PFAME	MEME	RES	LE
Yield of Liquid Hydrocarbon (Weight Percent)	71	62.5	68	58	64	58	57	69	64.5	68	65	67	67.5	71.5	70	73.5	73	67.5

Catalyst : Fluka Type 504C Alumina (pH 4.5)
 Carrier Gas/Flow Rate : Nitrogen Gas/120 ml per min
 Reaction Temperature : 510°C
 Reaction Pressure : 1 Atmosphere

In all cases there was no uncracked starting material in the hydrocarbon products i.e. representing 100% conversion.

PO - Palm Oil	PL - Pork Lard
CNO - Coconut Oil	BF - Beef Fat
CO - Corn Oil	MF - Mutton Fat
SO - Soya Oil	CF - Chicken Fat
SAO - Safflower Oil	PFA - Palm Fatty Acids
SNO - Sunflower Oil	PFAME - Palm Fatty Acid Methyl Esters
LO - Linseed Oil	MEME - Mutton Fat Methyl Esters
CO - Olive Oil	RES - Residue fraction from acid splitting of palm oil
PNO - Peanut Oil	LE - Light ends fraction from acid splitting of palm oil

- 13 -

TABLE 2 DISTILLATION CHARACTERISTICS OF CRUDE PETROLEUM SAMPLES AND LIQUID HYDROCARBONS
OBTAINED FROM THE CRACKING OF OILS AS SHOWN IN TABLE 1

Sample Boiling Point °C		PERCENTAGE DISTILLATE OBTAINED (VOLUME PERCENT)											
		PO	CNO	CO	SO	SAO	SNO	LO	OO	PNO	PL	BF	MF
150	12.5	5	8.5	6	18.5	17.5	13	17	11.5	14.5	10	9	9
200	22	25	22	19.5	30	29.5	25.5	31	26.5	26.5	23	20	20.5
250	40	47.5	39	43	46.5	46	41	45	42	41	37	34.5	35
300	70	73	64	65.5	69	70	66.5	71	69	62.5	60.5	61	61

Sample Boiling Point °C	PERCENTAGE DISTILLATE OBTAINED (VOLUME PERCENT)										
	PFA	PFAME	MFME	RES	LE	Tapis Crude	Shengli Crude	Arab Crude	Light Crude		
150	10	11.5	14.5	5	7	8	6	16			
200	20	26	28.5	11	19.5	17	11.5	27			
250	37	43.5	45.5	20	35.5	26.5	16.5	36.5			
300	66	66.5	71	59	57	40	25	49			

TABLE 3 YIELD AND DISTILLATION CHARACTERISTICS OF LIQUID HYDROCARBONS
OBTAINED FROM THE CRACKING OF OILS AND RUBBERS UNDER DIFFERENT CONDITIONS

Alumina (pH 4.5)															Alumina (pH 7)		Alumina (pH 9.5)	Alumina (pH 4.5) + 10% Merck Silica Gel 100	
CATALYST																			
OIL/RUBBER	PFA	PFA	PO	PO	PO	PO	PO	PO	PO	MP	MA	MPA	NR	CTRT	PFA	PFA	PFA	PO	
Carrier Gas Flow Rate 120/ml/min	H ₂	Ar	N ₂	Ar	He	H ₂	CH ₄	Ar	gas	No	N ₂	N ₂	N ₂	Ar	Ar	He	Ar	Ar	N ₂
Reaction Temperature	510	510	550	510	510	510	510	510	510	510	510	510	510	510	510	510	510	510	510
Yield of Liquid Hydrocarbons (weight percent)	63.5	67	70	69	67	66	36	57.5	64	61.5	64	64	66	51	52	61	62	57.5	
DISTILLATION OF HYDROCARBON PRODUCTS																			
Distillation Temperature °C																			
150	16	11	15.5	12	8.5	13.5	11.5	13	28	17.5	9	15.5	24	10	11	11	11	18	
200	29	22.5	29.5	22	18	28.5	20.5	25	45	34	26	30	62.5	36.5	21	22	22.5	33.5	
250	48	40.5	52	38.5	34	46.5	36.5	42	65.5	50	41	45.5	76.5	48.5	37.5	36.5	40.5	53	
300	72	69	78	65	59	69.5	60	68	84	69	64	65	87.5	69.5	68.5	68	69	76	

In all the above conversions were performed at 1 atmosphere pressure.
In all cases there was no uncracked starting material in the
hydrocarbon products.

- PFA - Palm Fatty Acids
- PO - Palm Oil
- MP - Mixture of palm oil, coconut oil, corn oil, soya oil,
safflower oil, sunflower oil, linseed oil, olive oil,
peanut oil and palm fatty acids.
- MA - Mixture of pork lard, beef fat, mutton fat and chicken fat.
- MPA - Mixture of MP and MA
- CNO - Coconut oil
- NR - Sunflower Oil
- CTRT - Commercial beava rubber
- CTRT - Car tyre rubber tube.



CLAIMS

1. A process for producing synthetic crude petroleum by catalytically cracking a biomass material (P) comprising
(a) a plant oil or a product obtained therefrom and/or
(b) an animal oil or a product obtained therefrom and/or
(c) a rubber using a catalyst comprising alumina with or without silica but excluding any zeolite content, the total amount of silica, if present, constituting a lesser amount by weight of the catalyst mixture.
2. A process according to Claim 1, wherein silica comprises no more than 25% by weight of the catalyst mixture.
3. A process according to Claim 2, wherein the catalyst is substantially wholly alumina.
4. A process according to any preceding claim, which is carried out in the presence of a carrier gas.
5. A process according to Claim 4, wherein the carrier gas comprises air or nitrogen or argon or helium or



hydrogen or a hydrocarbon obtained from petroleum refining and cracking operations.

6. A process according to Claim 5, wherein the said hydrocarbon carrier gas is methane.

7. A process according to any preceding claim, wherein the rubber (c) is natural rubber or in the form of a vehicle tyre or tube.

8. A process according to any preceding claim, wherein the said oils defined by (a) and (b) are not in anhydrous or pure form and have not been subjected to prior hydrogenation.

9. A process according to any preceding claim, wherein the said oils defined by (a) and (b) are triglycerides of fatty acids wherein the fatty acid moiety ranges from 4 to 30 carbon atoms.

10. A process according to Claim 9, wherein the said



- 17 -

fatty acids are saturated or contain 1, 2 or 3 double bonds.

11. A process according to any preceding claim, wherein the temperature of the catalyst is in a range of 300°C to 680°C.

12. A process according to Claim 11, wherein the temperature of the catalyst is in a range of 420°C to 550°C.

13. A process according to Claim 1 substantially as herein described and exemplified.
