

Pyrolysis of water-in-oil emulsions and vegetable oils in the presence of methylcyclohexane, analysed by GC / MS

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Abstract— In most tropical developing countries, the concern caused by agricultural overproduction is sometime enormous. In order to find a form of recovery of surplus production in Cote d'Ivoire, research has been undertaken to use vegetable oils as alternative to diesel. This work focused in the way of their chemical conversion related to campaign pyrolysis oils of palm, coconut, groundnut, cotton, and cabbage carried out between 350 and 600 °C in atmospheric pressure. A silica support is used in co-catalysis either with water or with methylcyclohexane. Liquid hydrocarbon yields reach 86%. A comparative study of the influence of homogeneous catalysts on the pyrolysis products was conducted and the contribution of the source of the starting triglycerides was highlighted. Recombinant esters were revealed as reaction intermediates.

Index Terms— continuous pyrolysis, hydrocarbons, mass balance; esters recombination.

I. INTRODUCTION

The fragility of the balance of trade of raw materials results in a shortage of foreign currency in developing countries mostly agricultural. This situation has caused worldwide strong interest in research into the use of biomass for energy purposes.

World production of petroleum and fats between 2007 and 2012 reached respectively 3.2 billion and 160 million tons a year. Prices during that period averaged \$ 650 USD per ton for oil and \$ 550 USD on average for oil [1].

Proposing to use these fats as fuel does not seem to be a rational decision. Yet economic and geopolitical arguments justify the use of this type of biomass for energy purposes.

First, petroleum delivered in the form of finished product is more expensive because it has to be sent along tracks. Thus, transport can double or triple the price of fuel.

The second factor is the dynamics of the market of oilseeds caused by periodic overproduction which cause the collapse of the course.

For a country like Côte d'Ivoire, third palm oil producer, decide to convert a decommissioned part of Straight Vegetable oils (SVOs) would guarantee farmers a floor price of oil to support agriculture without the consumer feels any increase in pump prices. So for this excess SVO can be hoisted to the rank of fuel would require that the proposed

wording is fully compatible with engines without mechanical editing.

In this work, we consider the path of chemical conversion that does not require adding product.

The first pyrolysis vegetable fats date from the 20s. They were conducted by many researchers including Gallo and Correlli [2], Mailhe et al. [3] who have studied the conversion of oils and vegetable fats and soaps into hydrocarbons. These experiments knew an important influx particularly during the colonial period.

After the oil crisis of the 70s, number of researchers [4, 5] pursued the thermal conversion of oil on various catalysts. At the end of these tries, the yield of the hydrocarbon cut was around 60%. The abundant gas was composed of hydrocarbon gases ranging from C1 to C5.

In most of this pyrolysis, catalysts efficiency was tested and models in chemistry were proposed to explain the reactional mechanisms [6, 7].

Others researchers turned in the way of the catalytic reforming of plant oil to produce hydrogen [8]. However, in the current stage, all these constructed models do not present predictive characters to allow reaching the pilot stage.

In addition to the previous work, a continuous pyrolysis campaign of different vegetable oils is undertaken in order to study the influence of water and methyl cyclohexane on the quality of the product and to propose a model to minimize coke and gas production.

The conversion of vegetable oils into biofuels by pyrolysis requires finding ways to reduce the amount of coke as pyrolysis gives a heavy and viscous residue [9]. This conversion will be done without using hydrogen known to be dangerous. To prevent the proliferation of coke precursors (alkylbenzenes, diolefins, and styrene mainly), methylcyclohexane is used as a simple hydrogen donor to implement. It is a model compound of cetane content in diesel which presents, contrary to the diesel oil itself, the advantage not to mask the peaks of the recombinants of the pyrolysis of oil in the mass chromatograms. Thus, the fillers used consist of crude oil, or a water-in-oil emulsion or a mixture of SVO and methylcyclohexane. Water and methylcyclohexane are not reactants but rather homogeneous catalysts in addition to the silica support.

II. MATERIALS AND METHODS

2.1. Materials

Biological materials

Different oils from Côte d'Ivoire are used: palm, copra, cabbage, cotton and groundnut. Their fatty acid compositions are summarized in Table I [10, 11].

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Fossil material consists of diesel fuel procured at a BP station in Paris (France).

Technical equipment

- A tubular reactor shown in figure 1, a tube furnace, a brand of HPLC pump JASCO PU 980i and a bottle of nitrogen at 200 bars.

Accessories

- Laboratory glassware, glass flow meter.

The analytical equipment consists essentially of a gas chromatography STAR 3400CX coupled to a mass spectrometer VARIAN-SATURN 4D.

2.2. Methods

The continuous pyrolysis consists of two main stages which are the sampling of oils and the pyrolysis process. Three types of sample are prepared for each oil: crude oil without additives, oil + 10% water and oil + 20% methylcyclohexane. Both ends of the reactor are packed with rock wool to prevent the silica support clog the pipes. The reactor is charged with a particle size of silica between 40 and 63 μ m. The sample is injected at a depth of 5 cm in the axis of the catalyst bed. This injection mode promotes better dispersion by capillary action of the oil in the bed.

At the nominal temperature of 400 °C, the silica is dried by scanning of the catalytic bed with nitrogen (0.5 to 1 mL / min) for ten to fifteen minutes. About five minutes after the start of injection, the reactor effluent is collected between 20 and 25 °C and analyzed.

III. RESULTS AND DISCUSSION

3.1 Pyrolysis balance

Pyrolysis balance is summarized in Table 3. The maximum rate is observed for pyrolysis temperatures of 550 °C. This result is consistent with the work of Marie Céline [12] which has experimented with zeolites. We performed a fast pyrolysis in which mass and heat transfer and phase transition phenomena play an important role according to Bridgwater [13]. Vegetable oils generally have a boiling point close to 230 °C [14]. Beyond this temperature, macromolecules of vegetable oils begin to break and decompose hydrocarbons. Conversion reactions tend to finalize around 550 °C.

Alkenes are disclosed as major products. They consist on average of 2/3 and 1/3 respectively for the monoalkenes and the polyalkenes.

The results show that pyrolysis conducted from 500 °C contain coke precursors such as aromatic and styrene that are harmful to fuel formulation. These results are consistent with those of Lu Qiang et al. [15] which stress that the presence of hydrocarbon aromatic in the reactor effluent requires a many attention due to their carcinogenic properties.

3.2 Effect of the nature of the oils on the pyrolysis product

To assess the influence of the nature of the oil, mainly characterized by the saturation rate, the mass distribution of the hydrocarbon compounds according to the oil saturation is

represented. Figure 2 shows the graphs for both conversion rates of 40% (a) and 75% (b) for copra (80.28% saturated), cabbage (73.61% saturated), palm (47.2% saturated) and groundnut (27.21% saturated).

Comparing these two graphs, it appears that:

- The proportions of pyrolysis compounds do not present the same trend for all oils. They therefore vary according to the nature of the oil.
- These proportions vary slightly depending on the exchange rate when we go to the same oil from 40% to 75% while maintaining the same trends. For all these oils in the proportion alkenes is strongly predominant, and oils to medium saturation rate (palm 47%) give a very low proportion for the other compounds.

Overall, the trends in the compound can be synthesized, when the conversion rate increases with oils saturation level, by:

- A decrease of alkenes;
- An increase of paraffins, alkylbenzenes, coke and hydrocarbon gases.

Alkenes of starting triglycerides would turn into alkybenzenes, styrene and subsequently coke. When defining the total hydrocarbons by the sum of the quantities of the hydrocarbon obtained in pyrolysis, figure 3 represents their evolution according to the conversion rate.

Points obtained from pyrolysis, without distinction of test conditions or the type of oils has a linear trend of total hydrocarbons based on the conversion rate. Searching correlation between pyrolysis products, it appears that, in general, there is no correlation with the degree of saturation, or with oils fatty acids distribution.

These results therefore show that the distribution of the proportions of hydrocarbon compounds is independent of the pyrolysis temperature, the degree of saturation and the conversion to hydrocarbon products.

3.3 Study of the influence of the homogeneous catalysts: water and methylcyclohexane

Figure 4 shows the comparative results of pyrolysis oil palm, groundnut and copra, in the presence of either water or methylcyclohexane or without additive.

The graphs highlight that in general that the conversion rate is higher with methylcyclohexane with water or no additive and the majority compounds are alkenes with predominance in monoalkenes.

Coke and hydrocarbon gases

The hydrocarbon gas mainly concern methane and ethylene. They are fundamental to the profitability since they constitute a net loss compared to the energy capacity of the initial charge. Coke formation generates the fouling of the reactor, thus it impacts the profitability of the process.

Gas proportions are less than 6% contrary to those published by Bridgwater [13] which gets 13% in the same condition of fast pyrolysis and temperature ranging between 500 °C and 530 °C.

Coke production rates we found are generally below 5% in contrast to the results of Bridgwater who earned more than double 12%. French, who performed a catalytic pyrolysis of biomass for biofuel production between 400 and 600 °C [6]

got between 22 and 31% of coke. The rate of coke production is thus due to the type of catalyst used and to the kind of vegetable oil.

For Guibet and Martin [16], the formation of deposits in the nose of the injectors is the first manifestation of combustion problems with vegetable oil from their thermal cracking or not accompanied by a slow oxidation.

In order to prevent the formation of deposits on the injector bodies of the conventional engine Hossain et al. [17] proposed that the engine is running prior to conventional fuel before crossing the pyrolysis oil.

Water

- Reduces remarkably the proportion of these $\pi(\pi)$ bonds holders unconjugated beyond 500 ° C.

- Reduces the proportion of hydrocarbon gas. As example with groundnut oil at 500 ° C, the rate is 9.40% (oil + 10% water) against 12.49% (for oil without additives) and 14.58 % (oil + 20% methylcyclohexane).

- With palm oil at 530 ° C, the rate is 10.50% (oil + 10% water) against 27.02% (for oil alone) and 16.23% (oil + 20% methylcyclohexane).

- With copra oil, we find that coke precursors rate is lower when no additive (4.04%). This rate is lower only in the case of oil + 10% water (6.34%) compared to the case of oil + 20% methylcyclohexane (6.67%).

Pyrolysis of heavy oils in the presence of water in the subcritical state was conducted by Chun Chun et al. [18] at a temperature close to that of breakage of the C-C bond. They concluded that the pyrolysis of heavy oils in water is dominated by an ionic mechanism and that water could approximately be regarded as an inert during the pyrolysis. However this result is not consistent with ours which show different conversion rates for oil without additives and in the case of water-in-oil emulsion.

Methylcyclohexane (mcc6)

Methylcyclohexane used as hydrogen donor effectively reduces the amount of coke. This result is in agreement with previous studies on the hydrocracking of vegetable oils led by Gusmao et al. [19]. They worked under pressures up to 200 bars hydrogen, which permit them to have a conversion of 100% of the load without coke production. Methylcyclohexane well acts as hydrogen donor to have results similar to those given hydrogen itself

- Promotes the production of gas. However, our rates are generally below 5% with methylcyclohexane against those of Barron et al. [20] who obtained 15% in the case of hydrocracking of vegetable oils of various hydrogenated catalysts.

It is therefore necessary to find a compromise between the amount of gas (total) and that of coke. For our pyrolysis campaign, this rate is around 50%.

3.4 Study of the impact of the residence time of the pyrolysis products

A second pass of palm, groundnut, and copra oils without additives is performed, and in the same temperature of 500 °C. That is to study the impact of the residence time in the reactor of the pyrolysis products. The results being similar; Figure 5 shows those of groundnut oil.

Figure 5-a, representing the mass chromatogram of crude oil, the starting fatty acids that make up the raw oil are revealed.

This is mainly fatty acids C16 saturated , C18 unsaturated, C18saturated.

1st pass: residence time: 5 min; conversion rate = 51.24%

Figure 5-b is the mass chromatogram of groundnut oil having undergone a pyrolysis at 500 ° C. We see the appearance of the characteristic peaks of absent fatty acids of the starting oil which are in fact fatty acid constructs and hydrocarbon synthesis products are paraffins, olefins, alkyl benzenes and styrenics.

2nd run: residence time: 10 min; conversion rate = 81.44%

The mass chromatogram of the 5-c reflects the sharp deterioration of the fatty acids starting on dilution in recombinats.

Compared to the spectrum of the crude oil (a), we find that the spectrum of the first pass to 500 ° C (b), the fatty acids of pure groundnut oil is practically found at the same retention time. These initial products of the oil are palmitic, oleic, stearic, linoleic, arachidic and behenic, elute respectively to 62; 65; 67; 68; 66; 72 and 78.5 minutes. The spectrum of the second pass at 500 ° C (c) meanwhile, highlights the partial or total fractionation most of these initial acids and their dilution in the recombinats. The sharp deterioration of the initial ester after the second passage is used to link the yield of hydrocarbons with the progress of the reaction. However, the large amount of coke after the second passage problem.

Influence of homogeneous catalysts on the recombination of esters

A representation of the proportion of recombined esters according to the conversion rate results for the three types of pyrolysis (without catalyst, with water, with methylcyclohexane), is given on the graphs of Figure 6.

Result show that methylcyclohexane is not a factor affecting recombination esters. But the addition of water reduces as evidenced by Figure 6, the recombination of the esters during pyrolysis. The proportions of the recombinant esters grow from the beginning of the pyrolysis up to a maximum value beyond which they fall. Let's consider the amplitude differences defined by:

$\text{écart_eau} = \text{recombination esters in the presence of water} - \text{recombination esters without additives}$

$\text{écart_mcc6} = \text{recombination esters in the presence of MCC6} - \text{recombination esters without additives}$

The representation of these differences depending on the pyrolysis conversion, gives the graphs of Figure 7

It appears that water reduces the rate of recombined esters during pyrolysis. The difference between the graph without catalyst and that obtained with water grows exponentially with the progress of the reaction as shown in figure 7.

The amount of recombinant esters grows from the reaction starting to a maximum before falling when the conversion rate approaches 100%. These recombinant esters are intermediate reactions which are converted into final products.

IV. CONCLUSIONS

Pyrolysis of vegetable oils between 350 ° C and 600 °C under atmospheric pressure both in the presence of water or methylcyclohexane leads to the formation of recombinant esters, paraffins, olefins, alkylbenzenes, styrenes, coke, hydrocarbon gas and CO₂.

The Conversion rates are higher with methylcyclohexane while the presence of water decreases the rate of coke precursors, reduces the gas, but it has no effect on the coke. Methylcyclohexane promotes the formation of gas but reduces the coke rate.

The recombinant esters have been revealed as intermediate reactions which are converted into final products. Alkenes revealed as major products consist on average of 2/3 and 1/3 monoalkenes polyalkenes.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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TABLES

Table 1: Fatty acid composition of vegetable oils (in% mass)

Carbon number	Fatty acids	Copra	Cabbage	Groundnut	Cotton	Palm
C8	caprylic	6,52	1,43	-	-	-
C10	capric	6,38	4,03	-	-	0,20
C12	lauric	27,73	28,9	0,04	0,03	0,62
C14	myristic	20,11	20,3	0,16	2,61	1,85
C16 :0	palmitic	13,37	14,04	13,23	20,82	31,26
C16 :1	pamlitoleic	0,74	-	0,14	0,23	-
C18 :2	linoleic	1,93	2,88	11,38	30,05	7,24
C18 :1	oleic	16	23,5	43,64	26,38	43,84
C18 :0	stearic	5,91	4,91	9,83	8,00	12,53
C18 :3	linolenic	-	-	3,32	5,70	1,61
C18 :3	α ₁ linolenic	0,62	-	3,04	5,13	-
C20 :0	arachidic	-	-	5,63	0,96	0,85
C20 :1	gadoleic	0,42	-	0,53	-	-
C22 :0	behenic	0,26	-	8,37	-	-
C22 :1	erucic	-	-	0,68	-	-
	% saturated	80,28	73,61	37,26	32,67	47,31

<< - >> : not determined

Table 2 : Pyrolysis mass balance (% mass)

Type oils	Conditions	paraffins	Monoal kenes	dialkenes	Alkylben zenes	styrenes	Recombi nedesters	Initial esters	CO ₂	Hydro carbon gas	Water	Coke
Groundnut	450°C	1.07	0.47	0.00	0.14	0.00	9.48	83.49	0.36	0.34	0.46	4.19
Groundnut	470°C	0.73	4.54	2.49	0.55	0.01	15.59	70.19	1.14	1.15	0.30	3.31
Groundnut	500°C	4.68	8.32	11.18	1.02	0.14	19.86	48.76	3.47	1.11	0.07	1.40
Groundnut	10% water at 500°C	2.71	6.62	8.69	0.66	0.08	11.73	64.66	3.11	0.00	0.02	1.71
Groundnut	20% mccc6 at 500°C	4.99	30.52	8.61	5.46	0.23	23.17	19.89	5.17	0.34	1.54	0.07
Copra	400°C	0.69	0.31	3.43	1.04	0.00	6.21	81.66	0.16	0.60	0.87	5.01
Copra	450°C	2.62	7.07	10.89	1.24	0.00	14.67	49.33	1.62	2.15	5.99	4.41
Copra	350°C	0.92	0.38	1.29	1.31	0.00	1.56	90.09	0.13	0.07	0.00	4.24
Copra	10% water at 400°C	1.44	0.15	0.51	1.28	0.00	0.79	90.85	0.11	0.00	0.36	4.50
Copra	20% mccc6 at 400°C	0.88	20.63	0.77	0.97	0.00	0.67	69.39	0.26	2.04	0.05	4.34
Copra	530°C	4.57	14.51	2.32	1.57	0.08	12.67	54.70	3.42	0.28	1.55	4.33
Copra	20% mccc6 at 530°C	12.57	19.34	3.50	2.82	0.24	24.30	28.31	3.99	1.34	0.39	3.20

Table 3 : Pyrolysis mass balance (% mass) (end)

Type oils	Condition s	paraffins	Monoal kenes	dialkenes	Alkylben zenes	styrenes	Recombi ned esters	Initial esters	CO ₂	Hydro carbon gas	Water	Coke
Copra	10% water at 545°C	6.28	18.58	3.61	2.63	0.04	14.31	45.71	4.56	0	1.21	3.06
Palm	400°C	1.69	0.17	2.54	2.16	0	17.48	73.17	2.28	0	0	0.5
Palm	500°C	1.76	24.66	10.04	1.35	0.03	10.08	45.06	3.64	1.12	0.53	1.72
Palm	530°C	5.25	30.23	22.33	2.9	0.6	11.84	15.96	3.18	2.1	2.29	3.31
Palm	20% mccc6 at 530°C	4	43.57	13.19	2.73	0.1	16.76	12.21	5.39	0.04	1.28	0.72
Palm	10% water at 530°C	3.46	19.46	8.19	1.98	0.02	8.55	49.53	2.69	1.58	1.4	3.15
Palm	10% water at 560°C	5.97	23.09	15.33	1.29	0.08	9.16	35.6	3.98	1.1	1.68	2.71
Palm	600°C	2.42	24.72	23.56	5.03	3.31	16.04	15.87	3.48	1.9	3.15	0.52
Cotton	460°C	0.45	0.94	2.07	1.43	0	6.84	84.11	0.55	0.21	0.13	3.26
Cotton	540°C	3.88	23.43	14.24	5.99	0.05	19.38	25.57	4.58	0.9	1.99	0
Cabbage	500°C	4.04	13.8	1.59	1.66	0.04	18.6	52.96	3.75	0.35	0.45	2.76
Cabbage	550°C	6.66	13.08	13.51	5.18	0.05	26.35	27.06	5.01	0.4	1.22	1.47

FIGURES

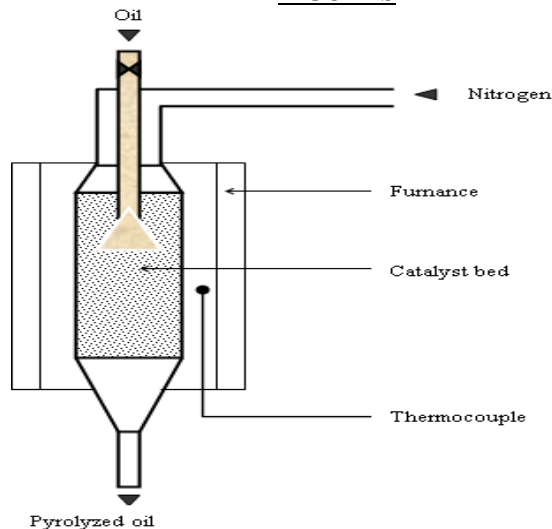
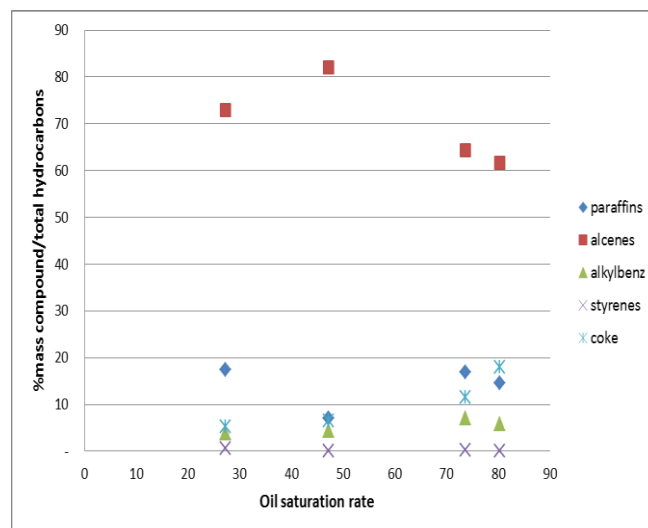
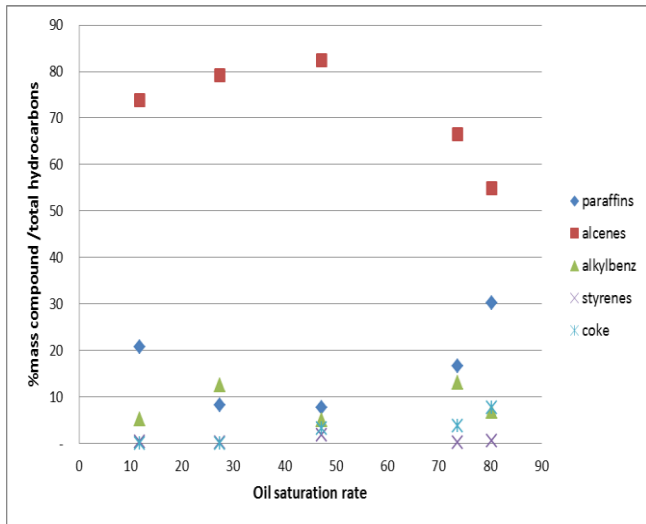


Figure 1: Block diagram of the reactor



(a)



(b)

Figure 2: The composition of the pyrolysis product in hydrocarbon compounds according to oils saturation level for conversion rate of 40% (a) and of 75% (b)

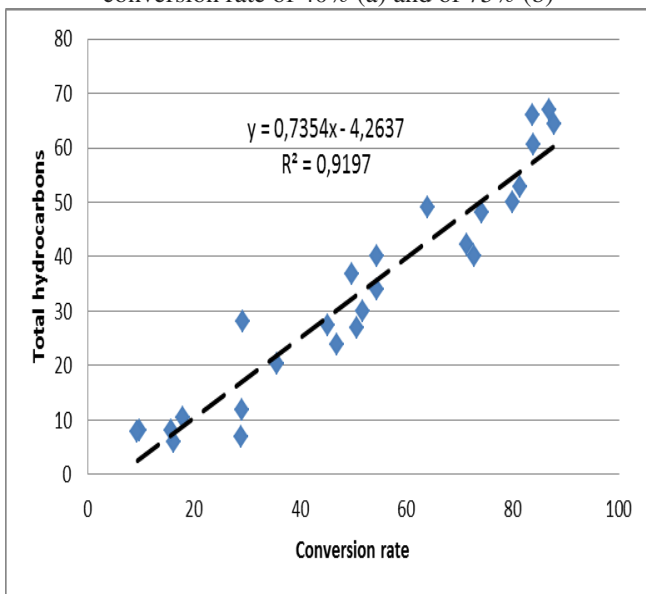


Figure 3: Evolution of total hydrocarbons based on the conversion rate

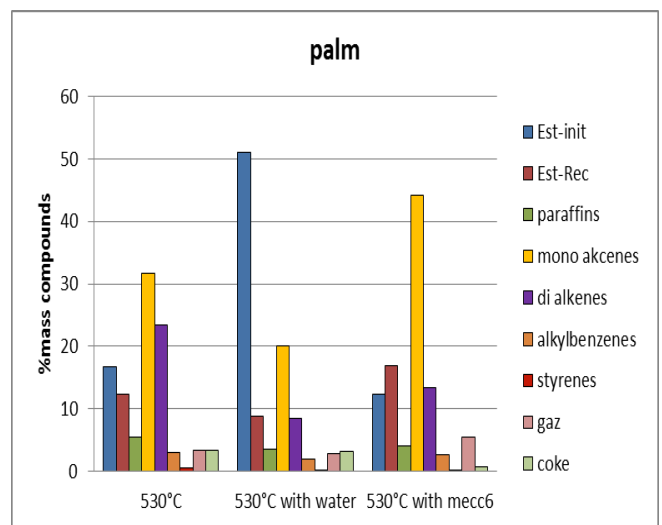
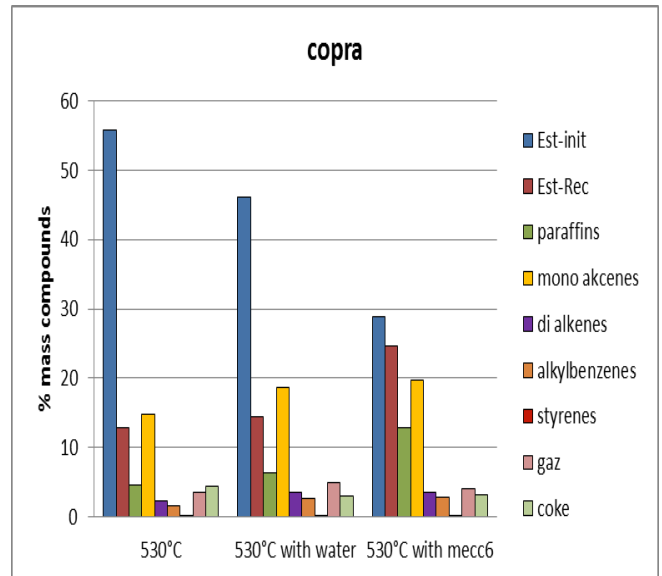
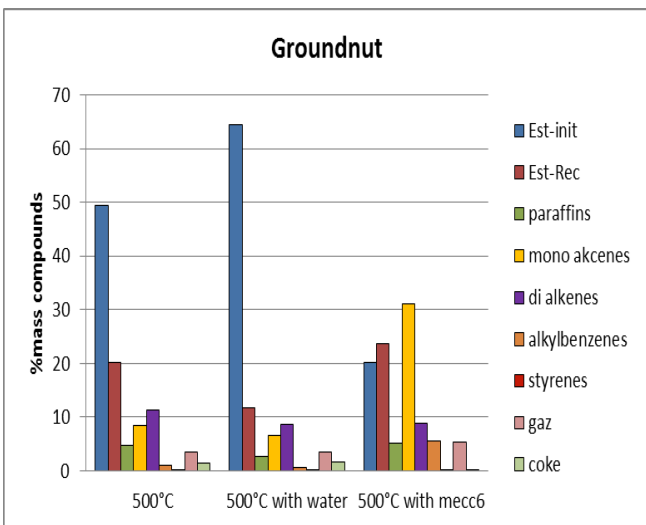
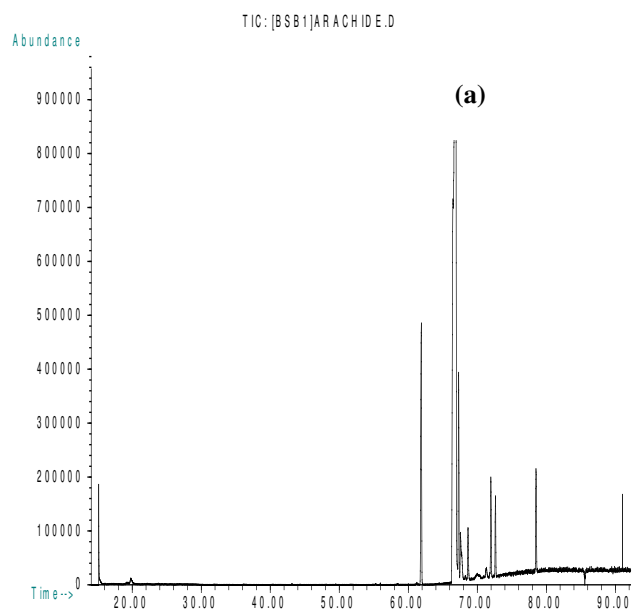


Figure 4 : Effect of water and methylcyclohexane on the pyrolysis products



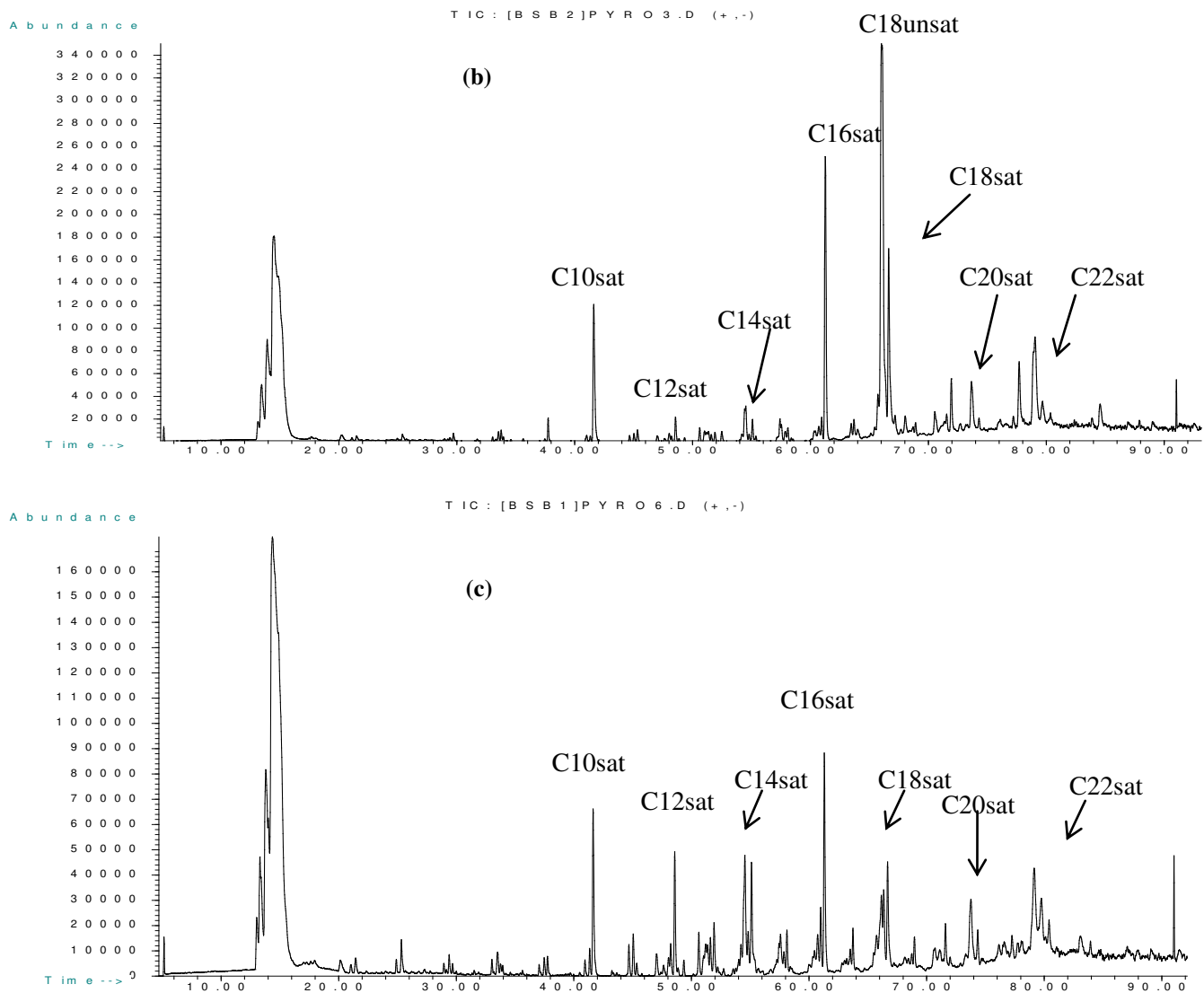


Figure 5: Mass Chromatograms of crude oil (a) and its pyrolysis compounds at 500 ° C (first passage (b) and second passage (c))

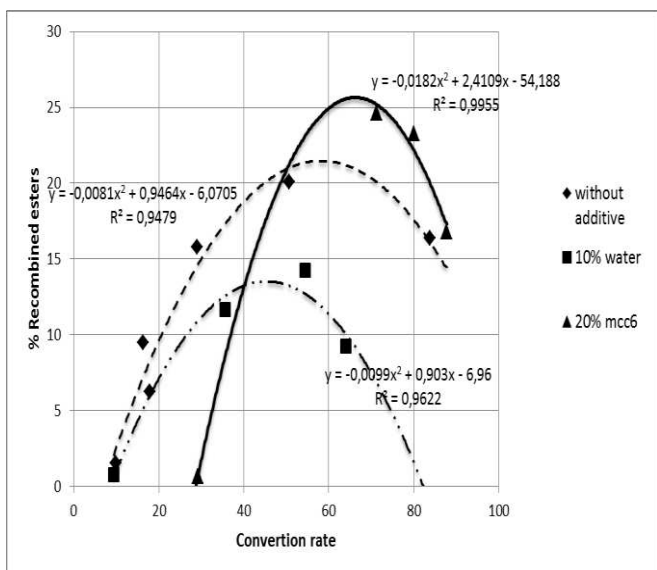


Figure 6: Influence of catalysts in homogeneous phase on recombinant esters: Case of groundnut oil between 400 and 530 ° C.

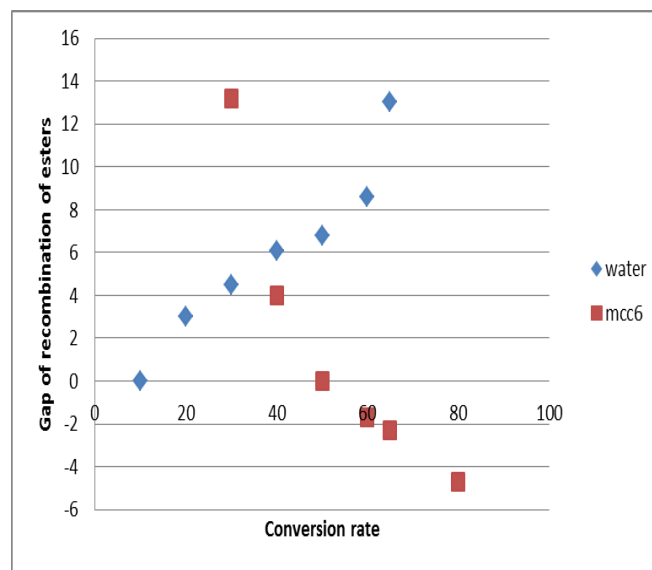


Figure 7: Differences in proportions of esters recombined between cases with and without additives