Σχολή Μηχανικών Περιβάλλοντος

Πυρόλυση φυτικών ελαίων και ζωικών λιπών κάτω από διαφορετικές συνθήκες για την παραγωγή ανανεώσιμων καυσίμων

Διπλωματική εργασία

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ΕΥΧΑΡΙΣΤΙΕΣ

Σε αυτό το σημείο, δε θα μπορούσα να παραλείψω να ευχαριστήσω την οικογένειά μου, που τόσο ένθερμα με στηρίζει σε κάθε μου απόφαση και κάθε μου βήμα.

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Tereza Kolaiti

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ABSTRACT

The need for energy is continuously increasing nowadays, if we take into account the rapid population growth and industrial development. Currently, this demand is satisfied partially by conventional energy resources and fuels such as coal, by 41,3%, natural gas, by 21,9%, nuclear, by 11,7%, oil, by 4,8% etc., which are also regarded responsible for a great deal of environmental problems, such as global warming or greenhouse emissions. As a result there has been the need of people to find ways to protect their natural environment and subsequently come up with more environmentally friendly solutions regarding energy development and exploitation. This is exactly where the issue of bioenergy emerges. Bioenergy is a renewable energy made available from materials derived from biological sources. One of the renewable resources that has gradually started to gain more and more interest is biomass.

In this project, experimental study and research has been carried out in order to create fuels out of natural products such as vegetable oils and animal fats. In the latest years, pyrolysis of biomass has become quite popular as a source for energy production and fuels. Through the process of pyrolysis, there is production of bio liquids and biofuels, which can be considered alternative and efficient materials in terms of fuels. With further treatment, their products can be adapted and added to refined petroleum products. More specifically, the pyrolysis of oils and fats allows the thermochemical conversion of triglycerides to substances with similar properties to those of gasoline.

As a result, the aim of this paper was to study and monitor the effect of some control parameters in the pyrolysis processes of vegetable and aviary oils, taken into

account their acidity, profiles, age so as to compare the conversion yields of the products produced with those of the biofuels.

ΠΕΡΙΛΗΨΗ

1. Εισαγωγή

Η ανάγκη για ενέργεια αυξάνεται συνεχώς στις μέρες μας, αν λάβουμε υπόψη την ταχεία αύξηση του πληθυσμού και της βιομηχανικής ανάπτυξης. Επί του παρόντος, η ζήτηση αυτή ικανοποιείται μερικώς από συμβατικές πηγές ενέργειας και καύσιμα, όπως ο άνθρακας, κατά 41,3%, το φυσικό αέριο, κατά 21,9%, τα πυρηνικά, κατά 11,7%, το πετρέλαιο, κατά 4,8%, κλπ, που επίσης θεωρούνται υπεύθυνες για ένα μεγάλο μέρος των περιβαλλοντικών προβλημάτων, όπως η υπερθέρμανση του πλανήτη ή το φαινόμενο του θερμοκηπίου. Ως αποτέλεσμα υπήρξε η ανάγκη των ανθρώπων να βρουν τρόπους για να προστατεύσουν το φυσικό περιβάλλον τους και στη συνέχεια να καταλήξει σε πιο φιλικές προς το περιβάλλον λύσεις, όσον αφορά στην ενεργειακή ανάπτυξη και εκμετάλλευση. Και εκεί ακριβώς είναι το σημείο όπου αναδύεται το θέμα της βιοενέργειας. Η βιοενέργεια είναι μια ανανεώσιμη ενέργεια και διατίθεται από υλικά που προέρχονται από βιολογικές πηγές. Μία από τις ανανεώσιμες πηγές ενέργειας που έχει ακτινικά άρχισε να αποκτά όλο και περισσότερο ενδιαφέρον είναι η βιομάζα.

Σε αυτήν την εργασία, η πειραματική μελέτη και έρευνα έχει διεξαχθεί για τη δημιουργία καυσίμων από φυσικά προϊόντα, όπως φυτικά έλαια και ζωικά λίπη. Τα τελευταία χρόνια, η πυρόλυση της βιομάζας έχει γίνει αρκετά δημοφιλής ως μέθοδος

για την παραγωγή ενέργειας και καυσίμων. Μέσω της διαδικασίας της πυρόλυσης, πραγματοποιείται παραγωγή βιοκαυσίμων και βιοελαίων, τα οποία μπορούν να θεωρηθούν εναλλακτικά και αποδοτικά από άποψη καυσίμων. Με την περαιτέρω επεξεργασία, τα προϊόντα τους μπορούν να προσαρμοστούν και να προστεθούν σε πετρελαϊκά προϊόντα. Πιο συγκεκριμένα, η πυρόλυση των ελαίων και των λιπών επιτρέπει την θερμοχημική μετατροπή των τριγλυκεριδίων σε ουσίες με παρόμοιες ιδιότητες με εκείνες της βενζίνης.

Ως αποτέλεσμα, ο σκοπός αυτής της εργασίας ήταν να μελετηθεί και να παρακολουθεί την επίδραση κάποιων παραμέτρων ελέγχου στις διαδικασίες πυρόλυσης των φυτικών ελαίων και των ζωικών λιπών, λαμβάνοντας υπόψη την οξύτητα τους, τα προφίλ, την ηλικία τους, έτσι ώστε να καταστεί εφικτή η σύγκριση των αποδόσεων μετατροπής των προϊόντων που παράγονται, με εκείνες των βιοκαυσίμων.

2. Πειραματικό

Το πειραματικό μέρος της εργασίας αποτελείτο από διεργασίες οι οποίες είχαν –σαφώς- στόχο στην χρησιμοποίηση πρώτων υλών (φυτικών ελαίων και ζωικών λιπών) προς την παραγωγή βιοκαυσίμων - βιοντίζελ.

Πιο συγκεκριμένα, τα φυτικά έλαια που χρησιμοποιήθηκαν ήταν: *ελαιόλαδο* και *πυρηνέλαιο*, ενώ ως ζωικό λίπος προτιμήθηκε το *λίπος κοτόπουλου.*

Ακόμα, είναι σημαντικό ν'αναφερθεί ότι προκειμένου να χαρακτηριστούν σε ένα βαθμό τα έλαια που χρησιμοποιήθηκαν κατά τη διεργασία της πυρόλυσης, πραγματοποιήθηκε έλεγχος της πυκνότητάς τους.

2.1 Εξοπλισμός

Η όλη πειραματική διαδικασία πραγματοποιήθηκε στο Universidade NOVA de Lisboa, στο τμήμα επιστήμης και τεχνολογίας, πιο συγκεκριμένα στο τμήμα Βιομάζας. Μάλιστα, ο εξοπλισμός που χρησιμοποιήθηκε κατά την διάρκεια των πειραμάτων για τη διαδικασία της πυρόλυσης ήταν ένας φούρνος-αντιδραστήρας πυρόλυσης, υψηλής πίεσης (brand Parr Instruments ®, UK) ο οποίος μπορεί να λειτουργήσει σε ένα εύρος θερμοκρασιών, έως 500 ° C και πιέσεων έως 300 bar.

Ο αντιδραστήρας αυτός, είναι χωρητικότητας 5 L, κατασκευασμένος από μέταλλο και πολύ ανθεκτικός σε κάθε είδους διάβρωση, πίεση καθώς και θερμοκρασία. Ακόμα, στην κορυφή του είναι τοποθετημένος ένας ψηφιακός ελεγκτής (Parr Instruments ® brand model 4848), ο οποίος καταγράφει τιμές για τρεις μεταβλητές: την θερμοκρασία, την ταχύτητα ανάδευσης και την πίεση στο εσωτερικό του αντιδραστήρα.

Τέλος, και ο αντιδραστήρας αλλά και ο ψηφιακός ελεγκτής είναι συνδεδεμένοι με έναν ηλεκτρονικό υπολογιστή, με τον οποίον είναι δυνατόν να δημιουργηθούν οι κατάλληλες συνθήκες, να τρέξει το πείραμα αλλά και να κρατούνται τα δεδομένα του πειράματος για κάθε χρονική στιγμή.

2.2 Η μεθοδολογία του πειράματος

Η πραγματοποίηση του πειράματος προαπαιτεί μία σειρά προετοιμασιών; των προετοιμασιών του πειράματος, του ίδιου του πειράματος, της συγκέντρωσης των προϊόντων και τελικά τον καθαρισμό του αντιδραστήρα.

2.3 Ο υπολογισμός της απόδοσης των προϊόντων πυρόλυσης

Για τον προσδιορισμό της απόδοσης των αερίων, υγρών και στερεών προϊόντων της πυρόλυσης χρησιμοποιήθηκαν σταθμικές μέθοδοι, αρχικά με το ζύγισμα του αντιδραστήρα και στη συνέχεια με απομόνωση των επιμέρους προϊόντων. Οι διαδικασίες παρατίθενται πιο συγκεκριμένα παρακάτω.

2.3.1 Χαρακτηρισμός των αέριων προϊόντων

Τα αέρια προϊόντα του πειράματος χαρακτηρίστηκαν μέσω αέριας χρωματογραφίας με ανιχνευτή θερμικής αγωγιμότητας. Αυτή η μέθοδος επέτρεψε την συγκριτική αξιολόγηση της σχετικής συγκέντρωσης των κύριων αερίων που υπήρχαν σε κάθε δείγμα, με τα άλλα αέρια που έχουν εγχυθεί προηγουμένως.

Ο χαρακτηρισμός των αέριων προϊόντων πραγματοποιήθηκε από το Chemical Laboratory – REQUIMTE του Universidade NOVA de Lisboa, του τμήματος Επιστήμης και τεχνολογίας

2.3.2 Χαρακτηρισμός του βιο-ελαίου

Επρόκειτο για τον πιο σημαντικό χαρακτηρισμό του πειράματος αλλά και τον λόγο εκπόνησης της παρούσας εργασίας. Διάφορες παράμετροι έπρεπε να αναλυθούν:

- Η πυκνότητα
- Στοιχειώδης ανάλυση και θερμιδική αξία

2.3.2.1 Απόσταξη των υγρών προϊόντων

Τα υγρά προϊόντα των πειραμάτων υποβλήθηκαν σε απόσταξη. Ο στόχος της διαδικασίας αυτής ήταν να ληφθούν δύο κλάσματα του υγρού, ενός πτητικού, το οποίο ελήφθη σε εύρος θερμοκρασίας μεταξύ 20 ° C - 150 ° C και ενός λιγότερο πτητικού κλάσματος, το οποίο ελήφθη σε μια θερμοκρασία που κυμάνθηκε μεταξύ 150 ° C - 200 ° C. Επιπλέον, υπήρχε ένα μέρος του υγρού που δεν μπορούσε να αποσταχθεί (ιλύς), διότι το σημείο ζέσεώς του ήταν προφανώς πάνω από τη μέγιστη θερμοκρασία απόσταξης.

Η συσκευή απόσταξης που έχει χρησιμοποιηθεί σε αυτό το πείραμα αποτελείται από αρκετά επιμέρους τμήματα. Αρχικά, υπάρχει ένας συμπυκνωτής, ο οποίος περιβάλλεται από ένα λουτρό ψύξης, στόχος του οποίου είναι ο έλεγχος της θερμοκρασίας συμπύκνωσης καθώς και την εξασφάλιση της πιο αποτελεσματικής συμπύκνωσης των πιο πτητικών συστατικών.

Στη δεξιά πλευρά του, ο συμπυκνωτής είναι συνδεδεμένος σε γυάλινη φιάλη, όπου εισάγεται το προς απόσταξη υγρό. Η φιάλη θερμαίνεται από ένα θερμαντικό μανδύα δύο αντιστάσεων. Στην κορυφή της φιάλης, τοποθετείται ένα θερμόμετρο το οποίο επιτρέπει τον έλεγχο και την καταγραφή των θερμοκρασιών κατά τη διάρκεια του πειράματος.

Στην αριστερή πλευρά του, ο συμπυκνωτής είναι συνδεδεμένος με ένα γυάλινο σωλήνα τριών εξόδων, όπου τοποθετούνται δύο μικρά γυάλινα φιαλίδια. Αυτά τα δύο φιαλίδια επιτρέπουν τη συλλογή των περισσότερο και λιγότερο πτητικών κλασμάτων (ελαφρύτερο και βαρύτερο). Αφού πραγματοποιηθεί η απόσταξη, τα δύο κλάσματα συλλέγονται, ζυγίζονται και αποθηκεύονται σε γυάλινα φιαλίδια.

2.3.2.2 Χαρακτηρισμός των υγρών προϊόντων για το GC-FID

Τα δύο αποσταγμένα κλάσματα στάλθηκαν στη συνέχεια προς χρωματογραφική ανάλυση στον GC-FID (Gas Chromatography- Flame Ionization Detection), έτσι ώστε να προσδιοριστούν το προφίλ του σημείου βρασμού και του αριθμού άνθρακα του υγρού.

2.3.2.3 Προετοιμασία του δείγματος

Πριν από την αποστολή των δειγμάτων για χρωματογραφική έγχυση, έπρεπε να υποστούν την κατάλληλη προετοιμασία. Τα δείγματα δε θα πρέπει να περιέχουν καθόλου νερό ώστε να εγχυθούν, και έτσι είναι απαραίτητο να ξηραίνονται πλήρως, διαφορετικά το νερό θα μπορούσε να επηρεάσει τα αποτελέσματα της συσκευής. Έτσι, με μία παστεριωμένη πιππέτα λήφθηκαν μερικές σταγόνες του ελαφρού κλάσματος και τοποθετήθηκαν σε έναν παστεριωμένο σωλήνα, στον οποίο είχε ήδη τοποθετηθεί ένα μικρό μέρος του βαμβακιού και θειικό νάτριο (Na_2SO_4). Έτσι, το βιο-έλαιο απομονώθηκε πλήρως από το νερό. Επιπλέον, προκειμένου να διασφαλιστεί η απομόνωση, ήταν απαραίτητο να αραιωθεί το δείγμα σε διχλωρομεθάνιο (CH_2Cl_2).

2.3.2.4 Συσκευή χρωματογραφίας

Κάθε χρωματογραφική ανάλυση πραγματοποιήθηκε στον αέριο χρωματογράφο Thermo Trace GC gas chromatograph200 system. Ο χρωματογράφος ήταν συνδεδεμένος με έναν υπολογιστή μέσω ενός, κατάλληλου για την ανάλυση, λογισμικού επιτρέποντας έτσι την αλληλεπίδραση μεταξύ του χρωματογράφου και του προγράμματος.

2.3.2.5 Χρωματογραφική ανάλυση

Η χρωματογραφική ανάλυση βασίζεται στο σημείο βρασμού του κάθε υδρογονάνθρακα. Εφόσον τα δείγματα εγχυθούν και παρατηρηθούν τα χρωματογραφικά τους προφίλ, μπορούν να οριστούν οι χρόνοι παραμονής του κάθε υδρογονάνθρακα κι έτσι μπορούν να οριστούν και τα χρονικά διαστήματα εντός των οποίων εκλύονται οι ενώσεις στο χρωματογράφο. Στη συνέχεια τα δείγματα εγχύνονται και τα χρωματογραφήματα συγκρίνονται με τα πρότυπα αυτών που υπάρχουν στην βιβλιοθήκη. Έτσι, αφού το χρωματογράφημα του δείγματος διαιρείται στα ίδια χρονικά διαστήματα, μπορεί να οριστεί ποιες ενώσεις έχουν την ίδια ποσότητα άνθρακα (με αυτές των προτύπων)..

2.3.3 Χαρακτηρισμός των στερεών προϊόντων

Κατά τη διάρκεια των πειραμάτων της πυρόλυσης, παρατηρήθηκε ο σχηματισμός στερεών προϊόντων μέσα στα βιο-έλαια. Είχαν τη μορφή βιο-ανθράκων και πλειοψηφία τους συλλέχθηκε από το ξύσιμο του αντιδραστήρα, μετά τη διεξαγωγή του πειράματος.

3. Αποτελέσματα

3.1 Πυρόλυση ελαίων και λιπών σε ατμόσφαιρα κενού

Η πυρόλυση του ελαιόλαδου, του πυρηνέλαιου και δύο ζωικών λιπών με διαφορετικά επίπεδα ελεύθερων λιπαρών οξέων πραγματοποιήθηκε σε ατμόσφαιρα

κενού, στις συνθήκες που αναφέρονται στον *Πίνακα 1*. Τα βιο-έλαια που προέκυψαν αποστάχθηκαν με σκοπό να απομονωθεί το πιο πτητικό καθώς και τα κλάσματα χαμηλού μοριακού βάρους που αντιστοιχούν στις επαρκείς ενώσεις για χρήση ως βιοκαύσιμα σε μηχανές εσωτερικής καύσης.

Πρώτες ύλες	t (min)	Απόδοση Πυρόλυσης (% w/w)			Απόδοση Απόσταξης (% w/w)		
		Αέρια	Υγρά	Στερεά	F1	F2	F1+F2
Ελαιόλαδο	20	15.0	84.5	0.5	25.7	39.6	65.3
	30	16.1	82.0	1.9	33.7	34.4	68.1
Πυρηνέλαιο	20	17.4	82.3	0.2	48.1	32.4	80.5
	30	44.0	55.2	0.8	17.7	48.4	66.1
Ζωικό λίπος (17%)	30	15.6	81.9	0.8	43.9	19.3	63.2

Πίνακας 1. Πυρόλυση των ελαίων και λιπών, σε ατμόσφαιρα κενού, σε 420 ^{o}C και απόσταξη των αντίστοιχων βιο-ελαίων: ο χρόνος αντίδρασης και η απόδοση των προϊόντων

Ακόμα, στα παρακάτω σχήματα παρουσιάζονται αντίστοιχα οι αποδόσεις στις διεργασίες πυρόλυσης και απόσταξης, κάθε ελαίου και λίπους.
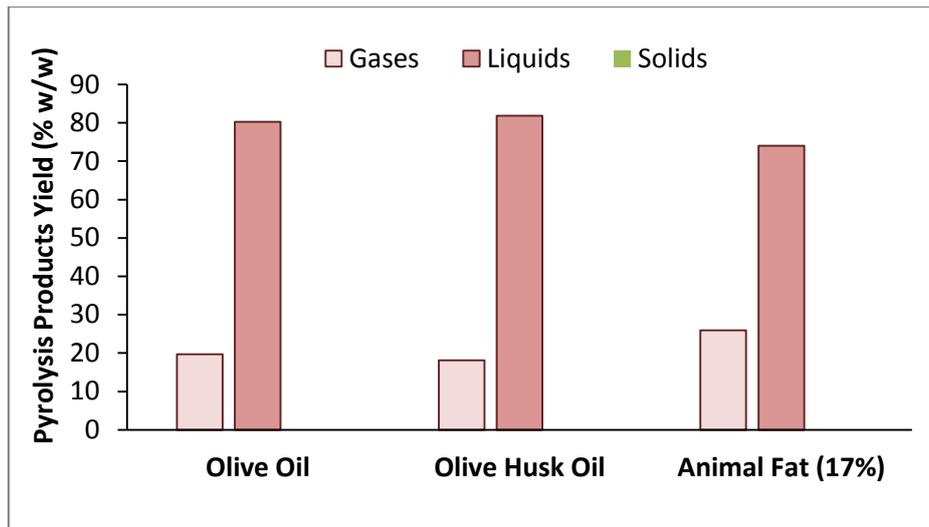
Σχήμα 1. *Πυρόλυση σε συνθήκες κενού των ζωικών λιπών και φυτικών ελαίων στους 420 ℃*
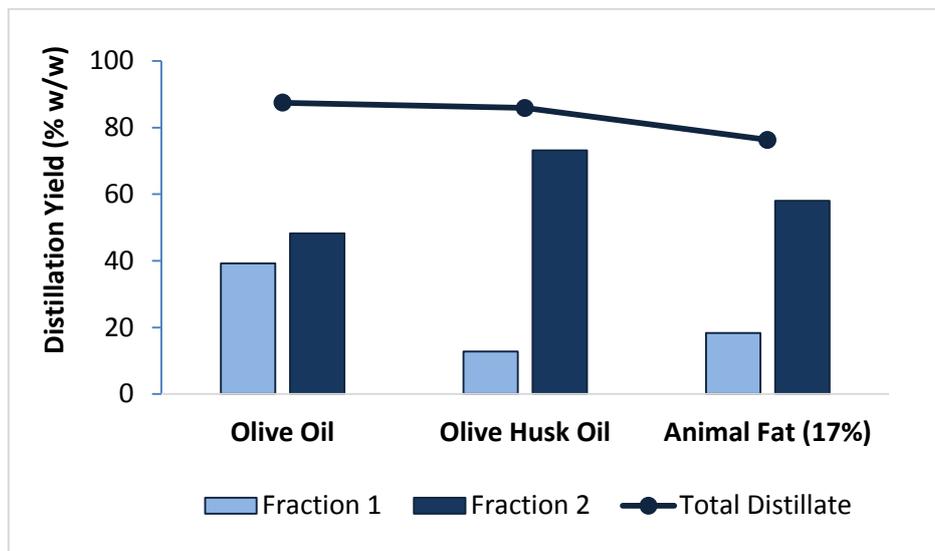
Σχήμα 2. *Απόσταξη του παραγόμενου βιο-ελαίου στους 420 ℃*

3.2 Πυρόλυση ελαίων και λιπών σε ατμόσφαιρα αζώτου (N₂)

Πρώτες ύλες	Αρχική πίεση (bar)	Αποδόσεις πυρόλυσης (% w/w)			Αποδόσεις απόσταξης (% w/w)		
		Αέρια	Υγρά	Στερεά	F1	F2	F1+F2
Ελαιόλαδο	3	19.7	80.3	0.0	39.3	48.2	87.4
Πυρηνέλαιο	3	18.1	81.9	0.0	12.7	73.1	85.9
Ζωικά λίπη (17%)	2.4	26.0	74.0	0.0	18.3	58.0	76.3

Πίνακας 2. *Οι αποδόσεις πυρόλυσης των ελαίων και λιπών, σε 420 ᵒC, κατά τη διάρκεια 10 min σε ατμόσφαιρα αζώτου και οι αποδόσεις απόσταξη των αντίστοιχων βιο-ελαίων*
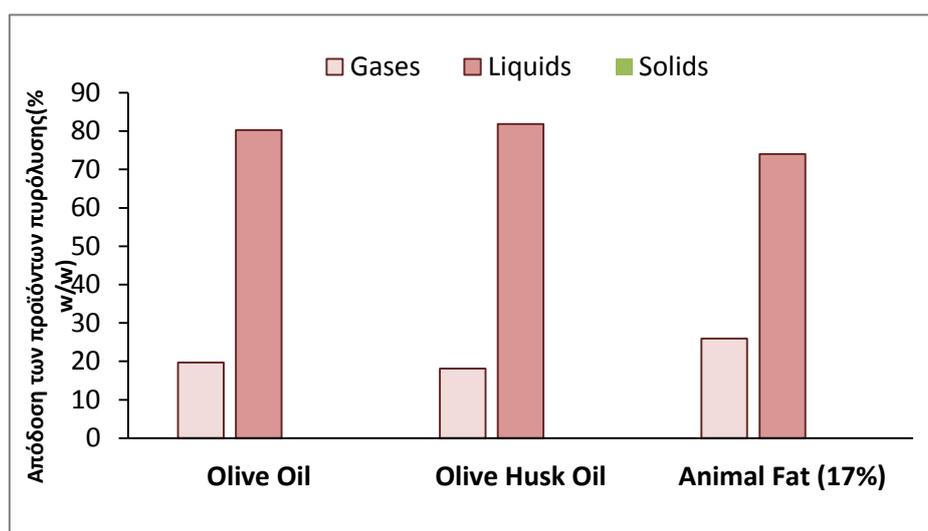
Σχήμα 3. *Πυρόλυση ελαίων και λιπών σε 420 ᵒC, 10 λεπτά σε ατμόσφαιρα αζώτου: Οι αποδόσεις των προϊόντων για τα αέρια, υγρά και στερεά.*
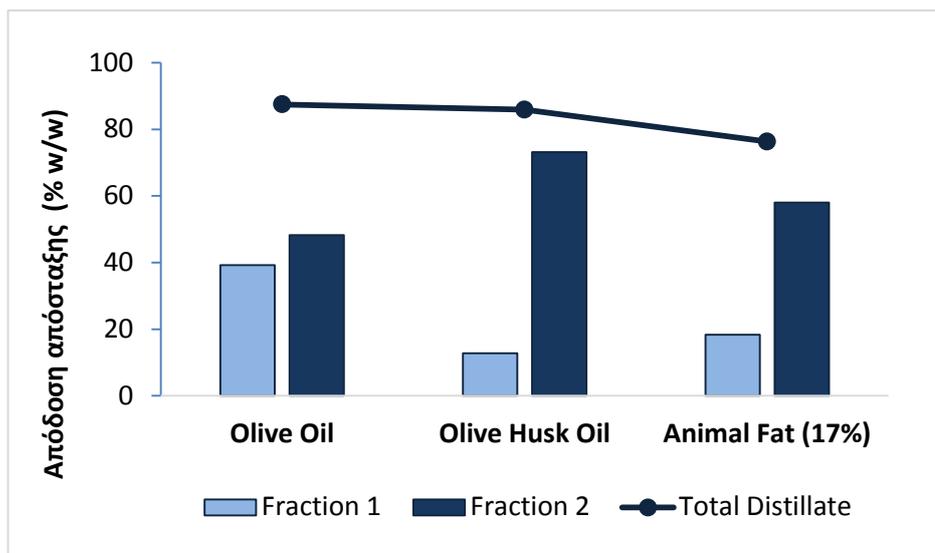
Σχήμα 4. *Απόσταξη των πυρόλυσης βιο-ελαίων που λαμβάνονται στο 420 °C, κατά τη διάρκεια 10 min υπό ατμόσφαιρα αζώτου.*

3.3 Πυρόλυση ελαίων και λιπών σε ατμόσφαιρα μεθανίου (CH₄)

Πρώτες ύλες	Αρχική πίεση (bar)	Χρόνος αντίδρασης (min)	Απόδοση πυρόλυσης (% w/w)			Απόδοση απόσταξης (% w/w)		
			Αέρια	Υγρά	Στερεά	F1	F2	F1+F2
Ελαιόλαδο	10	3	19.2	80.8	0.0	16.9	57.2	74.1
Πυρηνέλαιο	10	3	14.1	85.9	0.0	29.2	48.5	77.7
Ζωικά λίπη (17%)	10	3	18.7	81.3	0.0	18.1	40.4	58.5

Πίνακας 3. *Η απόδοση της πυρόλυσης των ελαίων και λιπών, σε 420 °C, σε 10 min σε ατμόσφαιρα μεθανίου και η απόσταξη των αντιστοίχων βιο-ελαίων.*
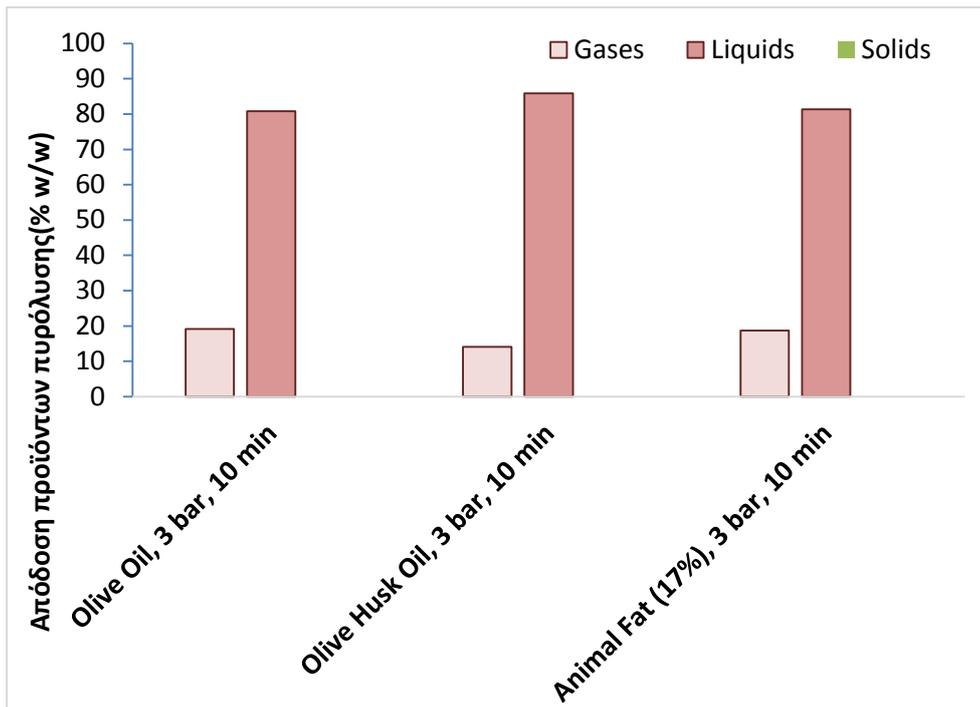
Σχήμα 5. *Απόδοση πυρόλυσης ελαίων και λιπών σε 420 °C, σε ατμόσφαιρα μεθανίου, για τα αέρια, υγρά και στερεά προϊόντα.*
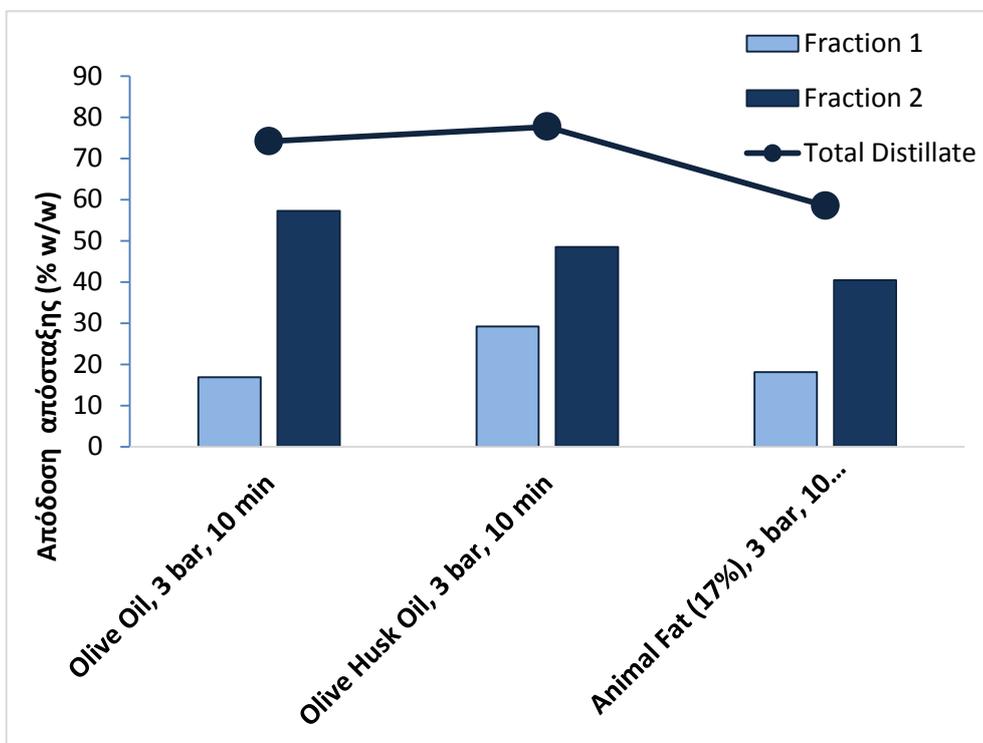
Σχήμα 6. *Απόσταξη των βιο-ελαίων που λήφθηκαν από την πυρόλυση σε 420 °C, σε ατμόσφαιρα μεθανίου.*

4. Συμπεράσματα

4.1 Γενικά συμπεράσματα

Όπως αναφέρθηκε προηγουμένως, ο σκοπός της μελέτης αυτής δεν ήταν να καθοριστεί εάν τα αποστάγματα που παράχθηκαν μέσω των πειραματικών διαδικασιών είναι βιοντίζελ, αλλά να εξεταστεί εάν δύο βασικές ιδιότητές τους είναι παρόμοιες με εκείνες του καθαρού diesel, δηλαδή οι συγκεντρώσεις μεθυλεστέρων και οι αποδόσεις απόσταξης.

Επιπλέον, μεταξύ των στόχων της παρούσας έρευνας ήταν να εκτιμηθεί ποια από τα τρία φυτικά έλαια και ζωικά λίπη, πληρούν τις προϋποθέσεις του diesel, καθώς επίσης και να προσδιοριστούν οι συνθήκες κάτω από τις οποίες αυτές οι ιδιότητες θα μπορούσαν να ικανοποιηθούν καλύτερα.

4.2 Συμπεράσματα για τα έλαια και τα λίπη

Γενικά, λόγω των διαφορετικών συνθηκών και ατμοσφαιρών, στις οποίες διεξήχθησαν τα πειράματα, είναι αρκετά δύσκολο να προσδιοριστεί ποιο είναι το έλαιο ή λίπος που ανταποκρίνεται καλύτερα στις ιδιότητες του diesel.

Έτσι, όσον αφορά στο πρώτο κλάσμα της απόσταξης, όλα τα έλαια και τα λίπη έχουν αρκετά παρόμοιες συγκεντρώσεις σε λιπαρά οξέα με μικρές παραλλαγές. Αυτό που μπορεί όμως να σημειωθεί, είναι ότι το πυρηνέλαιο παρουσιάζει τις υψηλότερες συγκεντρώσεις σε δύο ατμόσφαιρες (κενού και αζώτου). Όσον αφορά στο δεύτερο κλάσμα, τώρα, το πυρηνέλαιο πάλι κάνει τη διαφορά, στα - γενικά παρόμοια μεταξύ τους - προφίλ των λιπαρών οξέων διότι υπό την ατμόσφαιρα κενού, φθάνει σε συγκεντρώσεις λιπαρών οξέων μέχρι 23% για αριθμούς ανθράκων

από 11 έως 12. Συνολικά, ως μια συνολική απόδοση αποστάγματος, μπορούμε να παρατηρήσουμε ότι για το κλάσμα 2, τα βιοκαύσιμα που παράγονται φθάνουν αε αρκετά υψηλές αποδόσεις απόσταξης, φθάνοντας ακόμη και το 85%.

Ως αποτέλεσμα, το πυρηνέλαιο είναι το έλαιο που επιτυγχάνει την υψηλότερη απόδοση απόσταξης και στα δύο κλάσματα, σχεδόν σε όλες τις ατμόσφαιρες και ειδικά σε αυτήν του αζώτου.

4.3 Συμπεράσματα για τις πειραματικές συνθήκες

Ρίχνοντας μια ματιά στις αποδόσεις της απόσταξης, είναι προφανές ότι η ατμόσφαιρα αζώτου είναι η πλέον αποτελεσματική, φθάνοντας σε αρκετά υψηλές αποδόσεις απόσταξης μέχρι και 85%, οι οποίες είναι αρκετά υψηλές για βιοκαύσιμα. Επιπλέον, είναι προφανές ότι για το πρώτο κλάσμα, οι πλέον κατάλληλες ατμόσφαιρες είναι αυτές του μεθανίου και του κενού για το ελαιόλαδο, παρότι οι συγκεντρώσεις που φτάνει μέχρι και 30% και αυτή του μεθανίου για το ζωικό λίπος, πάλι με συγκεντρώσεις μέχρι και 33%. Η χρήση του μεθανίου έχει ως αποτέλεσμα μια σταθεροποίηση των συστατικών χαμηλότερου μοριακού βάρους του κλάσματος 1, δηλαδή με 8 έως 10 άνθρακες, για τα βιο-έλαια που λαμβάνονται από ζωικά λίπη (17%) ή το ελαιόλαδο, ενώ, στο δεύτερο κλάσμα απόσταξης, αυτό που μπορεί να συναχθεί από τα προφίλ των λιπαρών οξέων είναι ότι γενικά δεν φθάνουν υψηλές συγκεντρώσεις.

Σε αυτό το σημείο, είναι αρκετά σημαντικό να προστεθεί ότι οι διαφορετικοί χρόνοι πυρόλυσης, καθώς οι διαφορετικές πιέσεις της πυρόλυσης δεν επέφεραν σημαντικές επιπτώσεις στα παραγόμενα βιοέλαια . Κάποιες επαναλήψεις

πραγματοποιήθηκαν στο εργαστήριο, αλλάζοντας κάποιες μεταβλητές σε κάθε δοκιμή, όπως την πυρόλυση του ελαιολάδου σε συνθήκες κενού για 20 λεπτά αντί για 30 λεπτά ή χρησιμοποιώντας ζωικό λίπος 4,5% οξύτητας αντί για το 17% οξύτητας ή την εκτέλεση των πειραμάτων για το ζωικό λίπος σε 20 λεπτά αντί για 10 λεπτά. Σε κάθε περίπτωση, οι διαφορές στις αποδόσεις πυρόλυσης, οι αποδόσεις απόσταξης και τα προφίλ των λιπαρών οξέων ήταν ελάχιστες. Ως αποτέλεσμα, δεν υπάρχει λόγος στην εναλλαγή ή δοκιμή διαφόρων πειραματικών συνθηκών.

4.4. Προτάσεις για μελλοντική έρευνα

Στο σημείο αυτό, θα ήταν πολύ σημαντικό να γίνουν κάποιες προτάσεις για την περαιτέρω, μελλοντική έρευνα.

Όπως αναφέρθηκε προηγουμένως, λόγω της έλλειψης του διαθέσιμου εξοπλισμού, καθώς και χρόνου, δεν μπόρεσε να πραγματοποιηθεί στοιχειακή ανάλυση και χημική σύνθεση των παραγόμενων βιοελαίων. Έτσι, δείγματα των παραγόμενων βιοελαίων θα μπορούσαν να αποσταλούν στα κατάλληλα εργαστήρια για να καθοριστεί η ακριβής σύνθεσή τους και για να γίνει σύγκριση με τα Ευρωπαϊκά πρότυπα του βιοντίζελ 14214. Αυτή θα ήταν μια πολύ χρήσιμη και σημαντική προσθήκη για μελλοντική έρευνα.

Επιπλέον, και πάλι λόγω έλλειψης χρόνου και εξοπλισμού, δεν πραγματοποιήθηκε έλεγχος ποιότητας των παραγόμενων βιοκαυσίμων. Τα βιοκαύσιμα που παράγονται από τα δύο φυτικά έλαια και ζωικά λίπη δεν υποβλήθηκαν σε περαιτέρω ανάλυση σχετικά με τις ιδιότητές τους, όπως: εκτίμηση του ενεργειακού περιεχομένου τους, τη μέτρηση του pH, της περιεκτικότητάς τους σε

νερό. Αυτή είναι μία αρκετά σημαντική προσθήκη και θα πρέπει να ληφθεί πολύ σοβαρά υπόψιν για να πραγματοποιηθεί σε όλα τα βιοκαύσιμα που θα παραχθούν στο μέλλον.

Έτσι, αν και το αναβαθμισμένο βιοέλαιο θα μπορούσε να χρησιμοποιηθεί ως εναλλακτικό καύσιμο του λέβητα σε μηχανές εσωτερικής καύσης, ακόμα δεν μπορεί να αντικαταστήσει πλήρως τα ορυκτά καύσιμα και αυτό οφείλεται αποκλειστικά σε κάποιους περιορισμούς στην τεχνολογία και στο κόστος. Έτσι, είναι ένα αρκετά μεγάλο θέμα ο τρόπος με τον οποίο οι τεχνολογίες αναβάθμισής τους θα μπορούσαν να χρησιμοποιηθούν και να αναβαθμιστούν ώστε το βιοέλαιο από την πυρόλυση της βιομάζας θα μπορούσε να χρησιμοποιηθεί απευθείας, ιδιαίτερα για την περίπτωση του ζωικού λίπους (17% οξύτητας).

Τα ζωικά λίπη, γενικά, περιέχουν περισσότερες πρωτεΐνες και φωσφοακυλογλυκερόλες και αυτό οφείλεται στο γεγονός ότι είναι μεμβράνες ζωικών κυττάρων και έτσι παραμένουν εντός του κλάσματος λιπιδίων. Για το λόγο αυτό, μια διαδικασία αποκομμίωσης θα μπορούσε να πραγματοποιηθεί προκειμένου να εξαλειφθούν οι φωσφοακυλογλυκερόλες από τα λίπη, πριν από την παραγωγή βιοντίζελ. Μια πολύ αποτελεσματική διαδικασία, μέχρι στιγμής, είναι με τη χρήση 60% ορθοφωσφορικού οξέος, μετά από την οποία μπορεί να πραγματοποιηθεί φυγοκέντρηση έτσι ώστε να επιτευχθεί ο διαχωρισμός.

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Pyrolysis of vegetable oils and animal fats under different conditions for the production of renewable fuels

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1. INTRODUCTION

1.1 Biofuels

Right now, more than 35% of the world's primary energy demand is met by petroleum. According to the estimates of the International Energy Agency, this demand will reach much higher percentages in the years to follow; with the development of society, the consumption of fuels increasing continuously and is likely to double between 2000 and 2050. [Bulushev and Ross, 2011] This increase is paired with a decrease in the known resources of fossil fuels and an increase in greenhouse gasses emissions (of CO_2 especially) which are responsible for global warming. Due to the fact that most petroleum consumption nowadays is in internal combustion engines, the development of a light liquid fuel as an alternative to petroleum for use in existing internal combustion engines is quite urgent. [Ito et al., 2011] As a result, together with the recent rise in oil prices, along with growing concern about global warming caused by carbon dioxide emissions, biofuels have been regaining popularity. [http://www.greenchoices.cornell.edu/energy/biofuels/, June, 2015]

Biofuels are energy sources made from living things or even the waste that living things produce. They originate from a wide variety of sources and can be divided into four categories or generations.

- First generation biofuels: made from sugars, starches, oil and animal fats that are converted into fuel using specific, known processes and

technologies. They include biodiesel, ethanol, bioalcohols, and biogases.

- <u>Second generation biofuels:</u> made from non-food crops or agricultural waste, lingo-cellulosic biomass like switch-grass, willow or wood chips.

- <u>Third generation biofuels:</u> made from algae or other quickly growing biomass sources.

- <u>Fourth generation biofuels:</u> made from specially engineered plants or biomass that may have higher energy yields or lower barriers to cellulosic break down or are able to be grown on non- agricultural land or bodies of water.

So, their environmental benefits and the uncertainty concerning petroleum availability are among the basic reasons why, currently, biofuels have become more attractive. There are various ways of making biofuels, but generally, what is used the most are chemical reactions, fermentation, and heat to break down the starches, sugars, and other molecules in plants. The leftover products are then refined to produce a fuel that can be used by cars.

[http://www.greenchoices.cornell.edu/energy/biofuels/, June 2015]

1.2 Biomass

Biomass is a biological material derived from living or recently living microorganisms and as an energy source it can be either used directly (via combustion) or indirectly (after converting to forms of biofuel). It is mainly defined as any organic material that has the potential of being further transformed into energy.

Energy from biomass is considered to be quite durable and sustainable since it can ensure its own cycle and since it will be always produced and triggered by solar energy and radiation. Moreover, it is important to point out that biomass's cycle does not contribute to the accumulation of carbon dioxide in the atmosphere, for the fact that carbon dioxide that is liberated during the process is again immediately used by the plants in the process of photosynthesis.

By a chemical aspect, biomass is carbon based and composed of a mixture of organic molecules containing hydrogen, usually atoms of oxygen or nitrogen and also small quantities of other atoms (alkali, alkaline earth and heavy metals).

The carbon used to construct biomass is absorbed from the atmosphere as carbon dioxide (CO_2) by plant life, using energy from the sun. The primary absorption is performed by plants. The plant is generally broken down by microorganisms or buried. If broken down, it releases the carbon back to the atmosphere (mainly as carbon dioxide (CO_2) or methane (CH_4), depending on the conditions and processes involved or if buried, the carbon is returned to the atmosphere mainly as carbon dioxide (CO_2). Both these processes are considered part of the carbon cycle and have been happening on the Earth for as long as there have been plants on it.

The biomass that is used for energy can include a wide range of raw materials. There are five basic categories of material:

[http://www.biomassenergycentre.org.uk/portal/page?_pageid=75,15174&_dad=portal&_schema=PORTAL, June 2015]

- Virgin wood, from forestry, arboricultural activities or from wood processing

- Energy crops, high yield crops grown specifically for energy applications

- Agricultural residues, residues from agriculture harvesting or processing

- Food waste, from food and drink manufacture, preparation and processing, and post-consumer waste

- Industrial waste and co-products from manufacturing and industrial processes.

The greatest difference between biomass and fossil fuels is the one of time scale, since biomass takes carbon out of the atmosphere while it is growing, and returns it as it is burned. If it is managed on a sustainable basis, biomass is harvested as part of a constantly replenished crop. This is either during woodland or arboricultural management or coppicing or as part of a continuous programme of replanting with the new growth taking up CO_2 from the atmosphere at the same time as it is released by combustion of the previous harvest. This maintains a closed carbon cycle with no net increase in atmospheric CO_2 levels.

What is more, a basic advantage of biomass when compared to fossil fuels is that it is a renewable source of energy. Petroleum needs thousands of years under high temperature and pressure conditions to form, whereas the biomass is produced by various plants. Furthermore, as previously mentioned, the production and use of biofuels is neutral in terms of carbon dioxide (CO_2) emissions. Ecological balance is ensured, since the quantity of carbon dioxide (CO_2) produced during biomass

combustion is absorbed during its production, being thus alternative replacing conventional fuels. Last but not least, the cost and the potential reduction of carbon dioxide (CO_2) emissions in this way depends on the efficiency of energy conversion in the production and burning of biomass and on the type of fuel that it substitutes.

1.3 Biodiesel

Biodiesel fuels can be made from new or even used vegetable oils or animal fats, which are non-toxic, biodegradable and renewable resources. Recently, they have become more and more popular in fuel industries due to the fact that they are beneficial for the environment. [Bozbas, 2005]

Everything started when more than 100 years ago, an inventor named Rudolph Diesel designed the original diesel engine to run on vegetable oil. For his experiments, he used mainly peanut oil, as well as soybean, rapeseed and sunflower oil. He then noticed, that this kind of fuel could replace diesel oil in boilers and in internal combustion engines without any significant adjustments; much lower sulphate and carbon dioxide (CO_2) emissions, instead.

It is typically made by chemically reacting lipids with an alcohol, thus producing fatty acid esters. It is made to be used in standard diesel engines and is thus distinct from the vegetable and waste oils used to fuel converted engines. Moreover, it can be used in pure form or even blended with petroleum diesel (petrodiesel) in various proportions in both transport and heating. It has different solvent properties than petroleum diesel and will degrade natural rubber gaskets or

hoses in plain vehicles. Therefore, it is recommended to change or alter the fuel filters on engines and heaters shortly after having switched to a biodiesel blend.

A variety of oils can be used to produce biodiesel. The most common oils are virgin oil, rapeseed and soybean oil, whereas sunflower, palm oil, coconut oil as well as waste vegetable oils can be efficient, too. Waste vegetable oils are considered to be the best source of oils for biodiesel production, however their available supply is significantly less than the amount of petroleum-based fuels.

Moreover, animal fats (as by-products of meat production) including tallow, lard yellow grease, chicken fat and fish oil (rich in Omega-3 fatty acids) are highly preferred for the production of biodiesel. Algae, grown using waste materials such as sewage as well as sewage sludge are also quite attracting interest from major Waste Management companies because it is believed that renewable sewage biodiesel can be quite competitive with petroleum diesel on price.

1.3.1 Advantages of biofuels

Biofuels, have certain advantages and disadvantages in comparison to plain fossil fuels. More specifically, their advantages are [http://www.conserve-energy-future.com/advantages-and-disadvantages-of-biofuels.php, June, 2015] :

- Reduce Greenhouse Gases: Their most significant advantage is that biodiesels are quite clean fuels. That means that, subsequently, they produce up to 65% fewer emissions of greenhouse gases i.e. carbon dioxide (CO_2) in the atmosphere, while burning in contrast to plain fossil fuels, which when burnt, produce large amount of them. These greenhouse gases trap sunlight

and gradually cause the planet to warm. Moreover, the burning of coal and oil in plain fossil fuels is what increases the temperature. This is why biofuels are highly preferred around the world.

- Renewable fuels – reduced dependence on fossil fuels: Another undoubted advantage of biofuels is their renewability, which makes them unlikely to run out from the planet. This is a great property of theirs, due to the fact that a shortage of fossil fuels is predicted shortly in the future. The most common raw materials for biodiesel production are manure, corn, switch grass, soy beans, waste from crops and plants etc. These crops can be planted over and over again.

- Lower Levels of Pollution: Due to the fact that biofuels can be made from renewable resources, they cause much less pollution to the planet. As mentioned previously, they release lower levels of carbon dioxide (CO_2) as well as of other gases when burnt, which means their contribution to environmental pollution is not that important. Although their production creates carbon dioxide as a by-product, it is frequently used to grow the plants that will be converted into the fuel. So, the whole production process becomes self-sustainable.

- Cost: Currently, biofuels have the same price with gasoline. They are adaptable to current engine designs and perform achieving high yields in most conditions. This keeps the engine running for longer, requires less maintenance and brings down overall pollution check costs. With the increased demand of biofuels, they have a potential of becoming cheaper in future as well, especially with the prices of crude oil becoming so high in the years to follow.

- <u>Economic Security:</u> If a significant amount of people starts shifting towards biofuels and investing in them, then the dependence on the fossil fuels' imports will decrease. This would be a quite remarkable boost for all these countries and economies that do not have their own fossil fuels resources.

1.3.3 Disadvantages of biofuels

Even though, the use of biofuels as fuels can be very beneficial in many ways, it would be quite strange if there were not any drawbacks regarding their use. So, a focus on their negative side has to be performed. More specifically, the list of their most important disadvantages:

- <u>The high production cost:</u> Biofuels are quite expensive to produce in the current market, despite the benefits that they have. For the time being, the interest and capital investment being put into biofuel production is fairly low but has increasing intentions. If the demand increases however, then increasing the needed biofuel supply will be quite expensive. Such a disadvantage is still preventing the use of biofuels from becoming more popular nowadays.

- <u>Industrial pollution:</u> The carbon produced during burning of biofuels is significantly less than in conventional fuels. However, the process with which they are produced makes up for that. Their production is largely dependent on lots of water and oil. Large quantities of water are required to irrigate the biofuel crops and it may impose strain on local and regional water resources,

if not managed wisely. Furthermore, there is heavy soil erosion caused in areas that are meant for raw materials' growth.

- Use of fertilizers: Biofuels are produced from crops and these crops require the use of fertilizers so as to grow better. The use fertilizers can have harmful effects on the surrounding environment and involving the potential of water and groundwater pollution, since they contain nitrogen and phosphorus.

- Shortage of food: Due to the fact that biofuels are extracted from plants and crops that have high levels of sugar in them. These crops are used as raw material, and subsequently there is a high requirement for them. As a result, they take up much agricultural space from other crops, and that can create a sequence of problems. Even if, practically, this does not cause an acute shortage of food, it definitely puts pressure on the current growth of crops. One major worry expressed by farmers is that the growing use of biofuels may just cause a rise in food prices as well in the near future.

- Future rise in price: Last but not least, the current technology being employed for the production of biofuels is not as efficient as it should be. Scientists are engaged in developing better means with which we biofuels can be better extracted. However, the cost of research and future installation means that the price of biofuels will rise significantly. Even if now, biofuel prices are comparable with gasoline, thus feasible, it is believed that the constantly rising prices may make the use of biofuels as harsh on the economy as the rising gas prices are doing right now.

1.4 Purpose

The purpose of this study was to examine the efficiency of three different raw materials – olive oil, olive husk oil and aviary oil - for the production of sustainable fuels, with the process of pyrolysis. It was then examined if the bio oils produced by these raw materials were efficient enough, with properties and yields similar to those of contemporary fuels, so that they could be used as fuels.

Different pyrolysis conditions were performed for these oils. In the beginning, the three oils were pyrolyzed under vacuum conditions. Then, the following sequence of pyrolysis experiments was carried out under a nitrogen atmosphere and then under a methane atmosphere, so as to determine if any of those different atmospheres produce biofuels of better efficiency.

In the end of the experiments and after the produced fuels were distilled and later on examined in the GCMS device, a few comparisons were made between them and conclusions are made, so as to define the efficiency of the fuels, to review the experiment and propose further and future suggestions for improvement.

2. STATE OF THE ART

2.1 Biodiesel production processes

During the last decades much attention has been drawn into the development of biodiesel production technologies mainly due to fact that it biodiesels are renewable fuels with significantly reduced emissions compared to conventional diesel. Biofuel production using oil is not a new venture, after the first attempt dating from the late 19th century and was achieved by Dr. Rudolf Diesel, as mentioned previously.

The main advantages of plant oils, as raw materials for the production of biofuels are their immediate availability, their renewability, the lower content of sulfur and aromatic hydrocarbons and their biodegradability [Goering et al., 1982]. The main disadvantages of vegetable oils on the other hand, is their high viscosity, their low volatility and their ability to react with the unsaturated hydrocarbons.

Vegetable oils could be used directly as diesel fuels, but because of the higher levels of viscosity in comparison to ordinary diesel fuels, a modification of the engines is required [Kerschbaum et al., 2004]. The direct use of vegetable oils as fuels can replace only a small proportion of the transport fuels.

There are at least four ways in which the oils and fats can be converted into biodiesel through viscosity reduction, such as transesterification, fermentation, micro emulsification (mixing with a solvent) and pyrolysis.

Among all the proposed methods, the transesterification TG is by far the most common method, since it is the only process that directly leads to biodiesel products

and through which glycerin is produced; which is a product of high commercial value. The pyrolysis process of vegetable oils for the production of biodiesel is being investigated for over 100 years now and is the one that is being thoroughly studied in this paper.

2.1.1 Pyrolysis

Among the basic methods that have been developed in order to produce biofuels, pyrolysis is a significant one of them. Pyrolysis is a thermochemical decomposition of organic material in very high temperatures in the absence of oxygen, by causing the absolute and irreversible decomposition of the chemical composition and physical phase. During the pyrolysis process of biomass, gas, liquid and char are formed in proportions that depend on various conditions.

[Bridgwater, 2006] has classified the different modes of pyrolysis in which all biomass products are valuable and can be used. These are slow (of temperatures around 400°C), intermediate and fast (temperatures around 500°C) and last but not least, gasification (temperatures around 800°C).

It is thus, clearly shown that it is a technique prior of combustion and gasification, which is observed mainly in organic materials exposed in very high temperatures (starting from 200°). Its target is to form high energy density products in which biomass goes through physical and chemical changes. Of these products, the most important one is pyrolysis oil, which can be converted to fuel additives in a quite wide variety of ways. Depending on the conditions, the pyrolysis yield can reach up to 70-80% (in the optimum case). At this point, it should be noted that

pyrolysis liquid consists of 25% water. Pyrolysis of lower temperatures gives considerably higher concentrations of water, whereas those of higher temperatures lead to bigger formation of gases. [Bulushev and Ross, 2011]

In this series of experiments the two basic raw materials that were pyrolysed were poultry animal fats and vegetable oils: olive oil & olive husk oil more specifically.
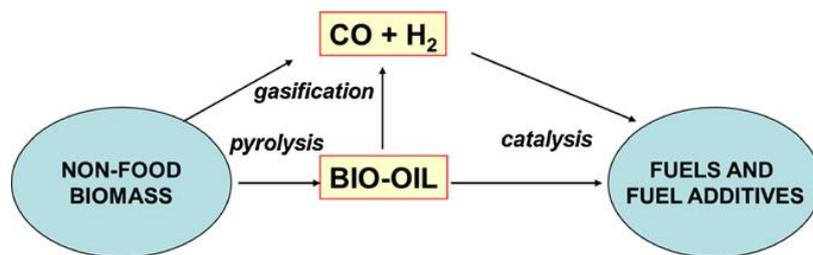
Image 1. Methods of biomass treatment and their products

2.1.1.1 Biomass pyrolysis

Biomass pyrolysis is a very complex procedure that involves simultaneous solid heat transfer, solid phase chemical reactions, liquid evaporation and thermal ejection, liquid phase reactions, mass transfer of vapours through the solid matrix and vapour phase reactions. It has emerged to be a very promising renewable energy technology aiming at the production of bio-oil. Being a thermochemical process, it takes place in a controlled environment at a quite high temperature levels (between 400°- $500^{o}C$), in the absence of oxygen. The produced vapour is very quickly condensed, so bio-oil and a permanent non- condensable gas (mainly consisting of CO, CO_2 and small fractions of H_2 and CH_4) are produced.

Many studies have already proven that biomass pyrolysis processes require careful control of the reactor temperature and residence times, so as to increase the yield of bio-oil. Furthermore, pyrolysis vapour is crucial to be removed quickly from the reactor hot zone so as to avoid secondary cracking relations. [Hassan et. al, 2015]

2.1.1.2   Pyrolysis of animal fats

As mentioned before, biodiesel is a very competitive, alternative fuel which has been attracting attention in the past years. In Europe, biodiesel production from virgin vegetable oils exceeds 3 million tons per year.

Regarding animal fats, they are primarily derived as by-products from meat animal processing facilities. Among main animal fats are tallow, lard and poultry fat. The use of these animal fat wastes as biodiesel feedstocks offer economic, environmental and food security advantages over the more commonly used edible vegetable oils. [Adewale et al.,2015] It is already well known that they contain quite larger free fatty acids (FFAs) than vegetable oils do. As a result, they require more complex production techniques and this often results in the production of biodiesel with a lower physical and chemical quality. [Alptekin and Canakci, 2012\ Ramírez-Verduzco et al.,2012]

It is crucial to mention, at this point, that animal fat waste contain quite large quantities of free fatty acids (FFAs) than vegetable oil waste do and as a result, it is quite possible to form soap. So, what has mostly been applied in the treatment of such fats is a pyrolysis method involving decarboxylation to the production of

biodiesel. Thus, it is considered that paraffins and olefins are formed. These paraffins and olefins are considered to have better both low-temperature properties and calorific values than FAMEs of equivalent carbon numbers. As a result, it is expected that biodiesel with significantly improved low-temperature properties can be produced, when waste oils and animal fats with high free fatty acid content are utilized. [Ito et al., 2011\ Santos et al., 2010]

By economic aspect, the processing of animal fat waste for biodiesel production can lower the production cost very close to conventional diesel's. Various treatment of waste animal fats, such as homogenous, heterogenous and enzyme catalysis as well as non-catalytic processes were considered with an emphasis on the influence of the operating and reaction conditions on the process rate and the ester yield. It was consequently determined that the (one- and two-step) homo-, heterogeneously catalysed processes had been very efficient for biodiesel production and that from now on, more research will be done on the application of enzymes, ultrasonic irradiation as well as microwaves and radio- frequency. In depth discussions were held regarding the optimization of the processes, the reactions' kinetics and possibilities for improvements. [Banković-Ilić et al., 2014]

2.1.1.3   Pyrolysis of vegetable oils

Some of the first biomass products that have been tested for biodiesel production, have been vegetable oils, since they can be found everywhere – crude or used – and they are subsequently, cheap.

Pyrolysis of triglyceride materials has been among the most popular fields of interest for researchers. A good example is when a review of pyrolysis processes was performed, comparing biomass and olive oil pyrolysis [Maher and Bressler, 2007]. Thermal cracking of vegetable oils was then concluded to be a quite effective representative method of producing bio-based products for use as fuels.

Moreover, it was figured out that the composition of the vapour phase obtained from pyrolysis of olive oil and other vegetable oils is close to that obtained from thermogravimetrical runs. The composition includes both gases – such as propene – and liquid – such as oleic acid, docosene and oktadecenal [Jansson et. al, 2012]. Another study carried out in 2009, analysed the thermal oxidative decomposition of olive oil by TG/DSC considering two processes in the first apparent peak, obtaining apparent activation energy between 27 and 145kJ/mol. [Vecchio et al., 2009]

On the other hand, there are not many tests carried out for olive husk oil. One of these has been to subject olive husk oil to direct and catalytic pyrolysis so as to obtain hydrogen rich gaseous products at specific temperatures and use them as fuels. It was noted that the total volume and yield of gas from both pyrolysis types increase with increasing temperature. [Caglar and Demirbas, 2000]

3. EXPERIMENTAL PART

The experimental design and procedures that took place during the experiments will be discussed and analysed, regarding the pyrolysis of the raw materials (both vegetable oils and animal fats), as well as their distillation and finally, characterization of the obtained products.

3.1 Characterization of raw materials

Our main goal in this series of experiments is to study the biofuel production of specific vegetable oils (olive oil, olive husk oil and coconut oil) as well as of specific animal fats (in this case aviary oils). The oil samples used were obtained from oil mills belonging to the Association of the Algarve oil producers. As a matter of fact, what was used was:

- <u>Olive oil</u>: it is an olive juice obtained from mechanical processes, which presents a high acidity that gives a bad taste

- <u>Olive Husk Oil</u>: it is obtained from the heating and treatment of olive pomace, with solvents

- <u>Aviary Oil (17% acidity)</u>: It is poultry fat, a kind sponsorship to our laboratory by a firm called AVIBOM

3.1.1 Density

In order to calculate the density of the oils, we determined their mass in the known volume of 2 mL of each crude oil, with a 2 mL pipette, in room temperature

(≈ 25°C). The method was performed in triplicate for each sample and the average density was taken into account in the end. The same method was performed, in calculating the density of the produced bio-oils.

The density was determined by using the equation:

$$\rho = \frac{m}{V}$$

Where,

- ρ, density (g/ mL)
- m, mass (g)
- V, volume (mL)

3.2 Pyrolysis samples

The main goal of this work is to study the biofuel production by pyrolysis of vegetable and aviary oils in different conditions (temperature, time of reaction, reaction with vacuum, Nitrogen or Methane), so as to determine their potential use as biofuels.

3.2.1 Equipment

The pyrolysis tests were carried out in the biomass laboratory of Universidade NOVA de Lisboa, department of Science and Technology and more specifically in the department of Biomass. The pyrolysis oven is a high pressure batch reactor, of brand Parr Instruments ®, UK, which can operate at a range of temperatures up to 500 ° C and pressures up to 300 bar.

3.2.1.1 The reactor

The reactor is a removable reactor of total capacity of 5 L, constructed of metal and it is highly resistant to corrosion, pressure and temperature. It consists of two lateral inlets at its top where two metal grips are clamped, thus allowing the moving of the reactor. On top of the reactor, a thin graphite ring is fitted through the grip to the body and lid of it and permits ensuring the tightness between the two components of the reactor, when the test is

Image 2. *The pyrolysis oven*

carried out. At the top of the reactor, 12 screws are located that can be closed and thus compress the reactor so as not to allow any possible leakage during the test and ensure the pressure of the systems remains the same. Last but not least, there are a stirring and a cooling system, a pressure and a temperature sensor as well as valves for the inflow and outflow of the gases produced.

3.2.1.2 Digital Controller

A digital controller (Parr Instruments ® brand model 4848) is connected to the reactor and they are both connected to a computer, thereby allowing the control of the experiment directly through the computer.

The controller consists of three digital panels. One is for temperature, another

one is for stirring speed and finally one for pressure. These panels allow us additionally to input the desired values we want our experiment to have.

Image 3. *The digital controller*

The panel of temperature indicates the temperature that exists inside the reactor and has a resolution of 1 ° C. This panel will act at the level of the oven temperature surrounding the reactor and will also act at the level of the cooling system by controlling the water inflow and outflow in the coil that is placed inside the reactor, thus maintaining the temperature constant and also serve in cooling the system by the end of each experiment.

The panel of stirring speed indicates the speed of the agitator inside the reactor during the experiment and has a resolution of 1 rpm.

The panel of pressure indicates the pressure inside the reactor and has a resolution of 0,1 bar.

As previously mentioned, the reactor and digital controller are both connected to a computer where it is possible to control the reactor as well as to make records and notes at an interval of 1 minute signing the testing time, temperature, pressure, stirring speed and gas flow inside the reactor so as to keep our experiment constantly updated and thus help the accuracy of the experiment.

3.2.2 Methodology of the experiment

The realization of the experiment requires e series of stages of preparation. These are the preparation of the experiment, the experiment itself, the collection of the products and finally the cleaning of the reactor.

3.2.2.1 Preparation of the experiment

Even before starting the test, it is necessary to perform a series of procedures so as to fully prepare the reactor for the experiment. These procedures depend on the experimental conditions:

- Weigh the empty cleaned reactor with its hands (our scale's accuracy is 0,1g)
- Weigh the desired amount of oil we want to test inside the reactor.
- Transfer the reactor to the main body of the pyrolysis oven
- Seal the reactor very well by tightening the screws
- Connect the digital controller with the computer
- Close very well all exits to the outside air and the gas inlet line to the reactor, leaving only the vacuum line open
- Ensure the entire system is working properly under vacuum by linking to the vacuum pump for some time (3-5 min)
- Close the vacuum line and open the gas inlet line at the same time. Then the reactor will slowly fill with gas and the digital controller will radially bring the system to the desired temperature and pressure values.

3.2.2.2 The experiment

Before each test we perform, the experimental conditions of time, pressure and temperature are defined:

- The temperature is set by the computer

- The heating button is connected to the stirring button while the digital controller regulates the agitation lever to the desired value.

- The reactor is then expected to reach the desired temperature. When it is reached, the temperature is automatically maintained and controlled through the cooling system.

- When the time of the experiment is reached, the oven as well as the agitation are turned off by the computer and the temperature inside the reactor is falling until it reaches a temperature similar to the ambient temperature (≈ 25 $^\circ$C). This is succeeded with the help of the refrigerating system.

Image 3. *The pyrolysis oven and the two nitrogen and methane tanks (blue).*

3.2.2.3 Collection of products

After the reactor will have reached a temperature really close to room temperature, we can proceed in the collection of products formed during the experiment:

- A sample of the gaseous products is collected carefully in a Tedlar bag of 5 L by pressure difference. Once it is collected, the air outlet is into the bag is closed and the air outlet to the room is opened so as the reactor is depressurised.

- The reactor can be then opened and immediately patched with a pre-weighted aluminium foil so as to minimize the contact between the liquid product and the air. Then the handles can be also placed.

- Afterwards, gravimetrical yield determination of gaseous, liquid and solid products is performed and then the reactor together with its handles, the liquid and the aluminium foil is weighed.

- The reactor is then transferred to a fume hood, where the liquid can be collected with a pipette and be stored in a suitable flask.

- In case solid products have been formed during the experiment, they are scratched out of the reactor and collected with a specific spatula into a pre-weighed glass vial.

3.2.2.4. Cleaning of the reactor

In the end, the reactor should be cleaned so as to be ready for a new experiment plus thus proper functioning will be ensured.

- The inside of the reactor has to be carefully cleaned with a tissue and some wet paper in order to remove every liquid remnants.

- The reactor's cover and the agitator should be also cleaned, therefore a large glass cup of acetone or hexane is placed underneath them and they are then left to dry.

3.3 Yield calculation of pyrolysis products

Gravimetric methods were used in order to determine the yield of gaseous, liquid and solid products. Weights before and after the experiment were recorded, as mentioned previously:

1. Initially, the weight of the reactor with its handles was recorded. Afterwards, the sample was added in the reactor. In case there was gas added in the experiment, its mass was also calculated. The new weight was recorded again. Thus, the difference between the two weights allowed the calculation of the reactants' weight.

2. After the test was carried out, the reactor was weighed again along with its handles, the liquid and solid products that were formed plus the aluminium foil that was used so as to avoid reaction between atmospheric air and the produced liquid. Again, the weight difference, before and after pyrolysis minus the weight of the aluminium foil, allowed the calculation of the weight of the gas formed during the experiment.

3. Afterwards, in order to measure the weight of the liquid products inside the reactor, we removed the liquid and weighed it again together with the handles and the aluminium foil. The difference in the weight would eventually give the weight of the liquid.

4. In the end, in order to calculate the weight of the solid products, they were removed (mainly by scratching) from the reactor and transferred to a pre-weighed glass vial. Then the vial was weighed again with the solids and the weight of the products was calculated by the difference.

Subsequently, with the weights of gaseous, liquid and solid products now given, the yield calculation of pyrolysis products could be carried out, in accordance to the equations:

$$m_{gases}(\%m/m) = \frac{gaseous\ products'\ weight}{total\ reactants'\ weight} \times 100 \quad (1)$$

$$m_{liquids}(\%m/m) = \frac{liquid\ products'\ weight}{total\ reactants'\ weight} \times 100 \quad (2)$$

$$m_{solids}(\%m/m) = \frac{solid\ products'\ weight}{total\ reactants'\ weight} \times 100 \quad (3)$$

3.3.1 Characterization of gaseous products

The gaseous products of the experiments were characterized by gas chromatography with a thermal conductivity detector. This method allowed us to evaluate by comparison the relative concentration of the main gases present in each sample, with the other gases that have been injected previously.

The characterization of the gases was performed at the Chemical Laboratory – REQUIMTE of Universidade NOVA de Lisboa, department of Science and Technology.

3.3.2 Characterization of the bio-oil

This characterization is the most important parts of biofuel making. Various parameters have to be analysed, such as density, elementary analysis

and calorific value.

However, due to both lack of time and equipment, only density calculations of the bio-oils were performed.

- Density

In order to determine the density of each liquid product the same method that is described before was performed, about measuring the density of crude oils (3.1.1).

Image 4. Some bio-oil samples

3.3.2.1 Distillation of the liquid products

The liquid products of the experiments were subjected to distillation. The aim in this procedure was to obtain two fractions of the liquid, one more volatile- obtained in a temperature range between 20° C - 150° C- and one less volatile fraction- obtained in in a temperature range between 150° C – 200° C. Moreover, there was a part of the liquid that couldn't be distilled (sludge) because its boiling point was obviously above the maximum distillation temperature.

The distillation device that has been used in this experiment consists of quite some parts. Initially, there is a condenser, surrounded by a cryogenic bath whose aim is to control the condensing temperature plus ensure the more effective condensation of the more volatile components.

On its right side, the condenser is connected to a glass flask where the to-be-distilled liquid is introduced. The flask is heated by a heating mantle of two resistances. On top of the flask, a thermometer is placed which allows the control and record of the temperatures during the experiment.

On its left side, the condenser is connected to a glass pipe of three exits, where two small glass vials are placed. These two vials allow the collection of more and less volatile fractions (lighter and heavier). After the distillation is finished, the two fractions are collected, weighed and stored in glass vials.

Moreover, the distillation yields of the fractions, are calculated by the following equations:

$$y_{1\ fraction}\ (\%m/m) = \frac{m_{1fraction}}{m_{liquid\ product}}\ x\ 100 \qquad (4)$$

$$y_{2\ fraction}\ (\%m/m) = \frac{m_{2fraction}}{m_{liquid\ product}}\ x\ 100 \qquad (5)$$

$$y_{sludge}\ (\%m/m) = \left(1 - \frac{m_{1fraction}+m_{2fraction}}{m_{\ liquid\ product}}\right) x\ 100 \qquad (6)$$

Image 5. *Distillation set, as described in 3.3.2.1.*

3.3.3 Characterization of the liquid products for GC-FID

The two distilled fractions were sent to GC-FID (Gas Chromatography- Flame Ionization Detection) analysis, so as the profile of boiling point and the carbon numbers of the liquid are determined.

*Image 6.* The distillation products still attached in the distillation system
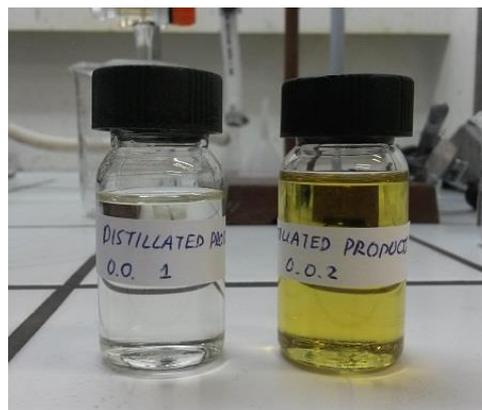
Image 7. The distillation products stored in suitable vials after their collection

3.3.3.1 Preparation of the sample

Before sending the samples for chromatographic injection, they should be prepared. The samples shouldn't contain any water in order to be injected, so it is necessary to be dried, otherwise the water could affect the results of the device. So a few drops of the light fraction was taken with a pasteurized pipette and was put into another pasteurized tube, in which a small portion of cotton and sulphate sodium (Na_2SO_4) was already placed. Thus, the bio-oil is completely isolated from water. Furthermore, in order to ensure that the isolation had been, it was necessary to dilute the sample in dichloromethane (CH_2Cl_2). More specifically:

- 0.1 ml of the oil we wanted to analyse was put on a small vial
- 2 ml of petroleum ether were added

- Some anhydrous sodium sulphate was added

- The liquid was stirred and checked in case the anhydrous sodium sulphate created small crystals. In the event of crystallization, a bit more of it was added so as to get a homogeneous mixture without any aggregate of anhydrous sodium sulphate

- The filter was prepared in a pasteurised pipette by placing a piece of cotton with great care, followed by a bit of anhydrous sodium sulphate and again another piece of cotton.

- The liquid was then filtered to a small flask for GC-MS and kept in a safe place so as to be protected from light

3.3.3.2 Chromatography apparatus

Every chromatographic analysis was performed on the Thermo Trace GC gas chromatograph 200 system. This chromatograph is connected to a computer via a, suitable for the analysis software allowing the interaction between the chromatograph and the program.

3.3.3.3 Chromatographic analysis

The chromatographic analysis is based on the boiling point of each hydrocarbon. After the samples are injected and by observing the chromatographic profile, the retention times of each individual hydrocarbon can be defined and thus the time intervals within which the compounds in the chromatograph are eluted can be defined. Afterwards the samples are injected and the chromatograms are

compared with the standard ones existing in the library. So, after the chromatogram of the sample is divided by the same time intervals, it can be defined which compounds have the same amount of carbons (as the standards). Thus, it is possible to quantify the percentage of each hydrocarbon using the equation:

$$\text{Number of carbons (\%)} = \frac{A_C}{\sum A} \times 100 \qquad (16)$$

Where,

A_C : sum of the areas of the carbon number range

$\sum_A$: total sum of the areas in the chromatogram

3.4 Collection of the solid products

During the pyrolysis tests, the formation of solid products was observed. They had the form of bio-carbons and their majority was collected by scratching the reactor, after the test was carried out.

4. RESULTS

The tests carried out for this paper are clearly shown on *Table 1*, below:

Atmosphere												
Raw material	Vacuum				Nitrogen				Methane			
		Time (min)	Pres sure (bar)	Tempera ture (°C)		Time (min)	Pres sure (bar)	Tempera ture (°C)		Time (min)	Pres sure (bar)	Tempera ture (°C)
Olive oil	T1	30	0	420	T4	10	3	420	T7	10	3	420
Olive Husk Oil	T2	30	0	420	T5	10	3	420	T8	10	3	420
Animal fat (17%)	T3	30	0	420	T6	10	3	420	T9	10	3	420

Table 1. Tests carried out

4.1 Characterization of the raw materials

At this point, it would be very useful to present a few things regarding the free fatty acid profiles of the raw materials that have been used for the experiments:

- **Olive oil**

Fatty acid	Chemical structure	Composition (%)
Palmitic acid	C16:0	10
Stearic acid	C18:0	5
Oleic acid	C18:1	80
Linoleic acid	C18:2	4
Linolenic acid	C18:3	1

Source: http://www.oliveoilsource.com/page/chemical-characteristics

Table 2. Olive oil Fatty Acid Profile

- **Olive husk oil**

Fatty acid	Chemical structure	Composition (%)
Myristic acid	C14:0	0.03
Palmitic acid	C16:0	13
Palmitoleic acid	C16:1	0.94
Margaric acid	C17:0	0.07
Heptadecanoic acid	C17:1	0.15
Stearic acid	C18:0	3
Oleic acid	C18:1	70
Linoleic acid	C18:2	11.5
Linolenic acid	C18:3	0.73
Arachidic acid	C20:0	0.33
Gadoleic acid	C20:1	0.08
Behenic acid	C22:0	0.16

Table 3. Olive husk oil Fatty Acid Profile

[Source: Ουαχάμπ, 2011]

- **Aviary oil**

Fatty acid	Chemical structure	Composition (%)
Myristic acid	C14:0	0.5
Palmitic acid	C16:0	24
Palmitoleic acid	C16:1	5.8

Stearic acid	C18:0	5.8	
Oleic acid	C18:1	38.2	
Linoleic acid	C18:2	23.8	
Linolenic acid	C18:3	1.9	

Table 4. *Animal fat (17%) Fatty Acid Profile*

[Source: Ito et al., 2012]

Parameter	Unit	Min	Max	Specification EN 14214:2012
Density at 15 k^{o}C	kg/m^3	860	900	EN ISO 12185
Viscosity at 40 ^{o}C	mm^2/sec	3.5	5.0	EN ISO 3104
Flash point	^{o}C	101	-	EN ISO 3679
Sulfur content	mg/kg	-	10.0	EN ISO 20846
Cetane number	-	51.0	-	EN ISO 5165
Sulfated ash	% m/m	-	0.02	ISO 3987
Water content	mg/kg	-	500	EN ISO 12937
Total contamination	mg/kg	-	24	EN ISO 12662
Copper strip corrosion	Rating	Class 1	Class 1	EN ISO 2160
CFPP	^{o}C	-	13	EN 116
Cloud point	^{o}C	-	16	EN 23015
Ester content	% m/m	96.5	-	EN 14103
Linoleic acid methylester	% m/m	-	12	EN 14103
Polyunsaturated methyl esters (>4 double bonds)	% m/m	-	1	EN 15779
Oxidation stability at 110°C	h	8	-	EN 14112
Acid value	mg KOH/g	-	0.50	EN 14104
Iodine value	g iodine/100g	-	120	EN 14111
Monoglyceride content	% m/m	-	0.700	EN 14105
Diglyceride content	% m/m	-	0.200	EN 14105
Triglyceride content	% m/m	-	0.200	EN 14105
Free glycerol	% m/m	-	0.020	EN 14106
Total glycerol	% m/m	-	0.250	EN 14105
Phosphorous content	mg/kg	-	4.0	EN 14107
Metals I (Na/K)	mg/kg	-	5.0	EN 14108
Metals II (Ca/Mg)	mg/kg	-	5.0	EN 14538
Methanol content	% m/m	-	0.20	EN 14110

Table 5. Biodiesel 14214 *European Standards*

[Source: Melero et al., 2010]

Fatty acid	Chemical structure
Lauric acid	C12:0
Myristic acid	C14:0
Palmitic acid	C16:0
Palmitoleic acid	C16:1
Stearic acid	C18:0
Oleic acid	C18:1
Linoleic acid	C18:2
Linolenic acid	C18:3
Arachidic acid	C20:0
Eicosenoic acid	C20:1
Behenic acid	C22:0
Eurcic acid	C22:1

Table 6. Biodiesel Fatty Acid Profile
[Source: Ουαχάμπ, 2011]

4.2 Pyrolysis of oils and fats under a vacuum atmosphere

The pyrolysis of olive oil, olive husk oil and two animal fats with different levels of free fatty acids were performed under a vacuum atmosphere, at the conditions indicated in *Table 1*. The resulting bio-oils were distilled in order to isolate the more volatile and low molecular weight fractions that correspond to the compounds adequate for use as biofuels in internal combustion engines.

Raw Materials	t (min)	Pyrolysis Yields (% w/w)			Distillation Yields (% w/w)		
		Gases	Liquids	Solids	F1	F2	F1+F2
Olive Oil	30	16.1	82.0	1.9	33.7	34.4	68.1
Olive Husk Oil	30	44.0	55.2	0.8	17.7	48.4	66.1
Animal Fat (17%)	30	15.6	81.9	0.8	43.9	19.3	63.2

Table 7. *Vacuum pyrolysis of oils and fats, at 420 ^{o}C and distillation of the corresponding bio-oils: reaction time and product yields.*
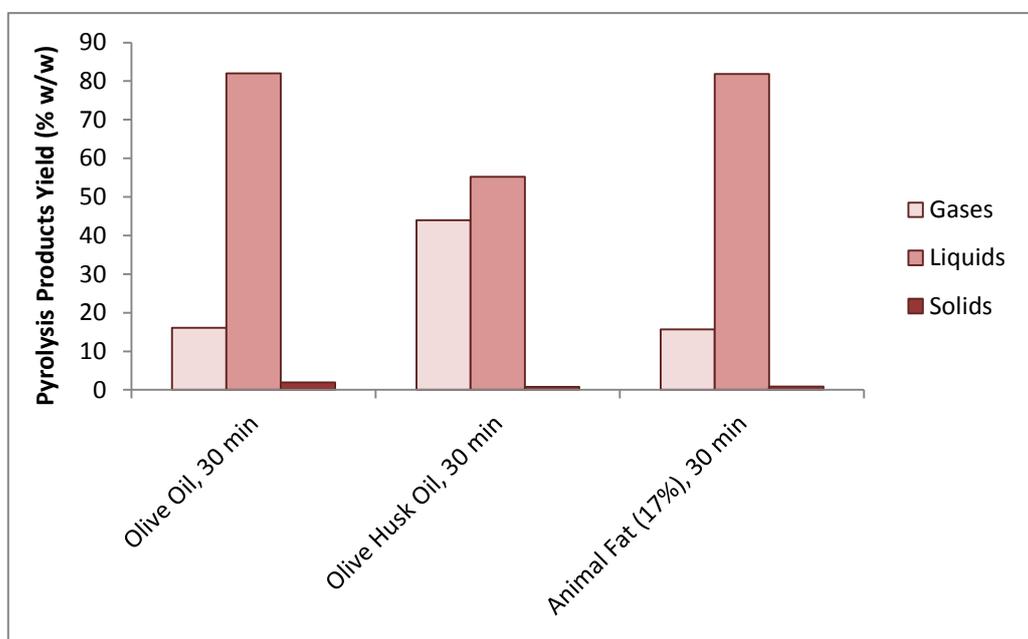
Figure 1. *Vacuum pyrolysis yields of oils and fats at 420 °C*

The thermochemical decomposition of the liquid raw materials is mainly followed by the gas products yields since the liquid products and the non-reacted oils and fats are miscible.

The gas products' yield increases with the increase in the pyrolysis time from 20 min to 30 min, especially for the olive husk oil.
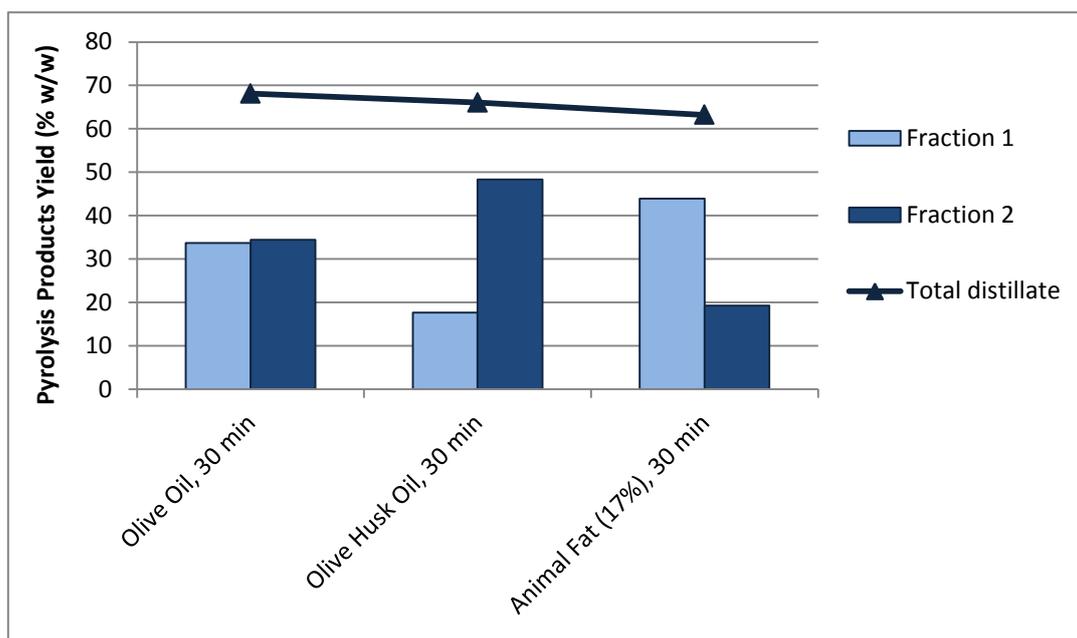
Figure 2. *Distillation yields of the pyrolysis bio-oil obtained at 420 ℃, under vacuum*

The total distillate yields of the vegetable oils and the animal fats are comparable except for the olive husk bio-oil that is richer in volatile components. The increase in the acidity of the animal fat led to an increase in the formation of lighter pyrolysis products (gases and fraction 1 components). Increasing the pyrolysis time of olive oil resulted in a higher content of *fraction 1* in the corresponding bio-oil.

The bio-oil obtained from the pyrolysis of olive husk oil during 30 min contains a lower concentration of fraction 1 components because they were converted in gas products.

4.2.1 Composition of the Distilled Fractions

The lighter fractions (F1) of the distillates were obtained in a range from room temperature to 150 °C while the heavier fractions (F2) were isolated in a temperature range from 150 °C to 250 °C with minor variations from these temperatures.

The distilled fractions were analyzed by gas chromatography and mass spectrometry and the main linear alkanes present in the distilled bio-oil were identified. The chromatographic profiles of the two distilled fractions from the bio-oil produced with olive oil at 420 °C and 30 min are presented in *Figure 3*.
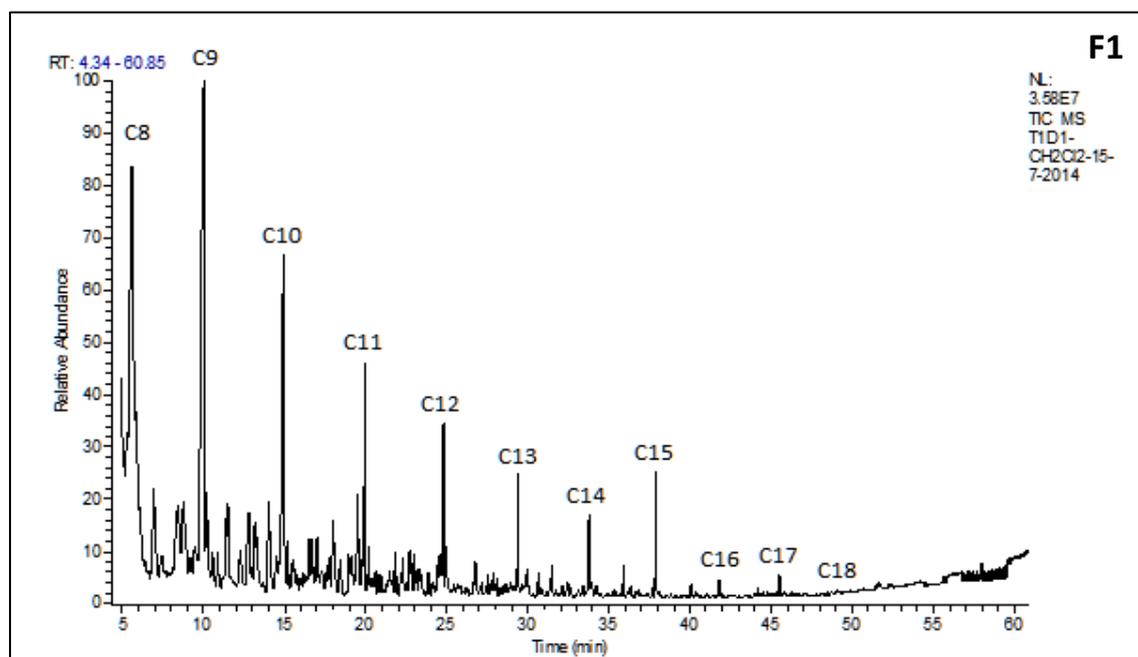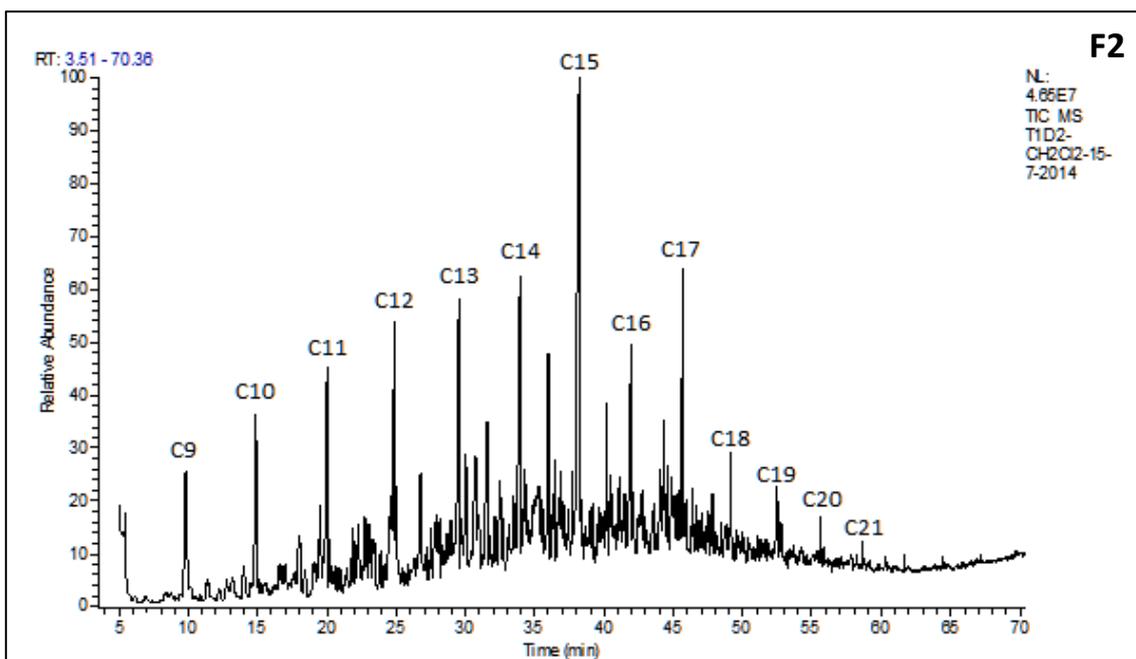
Figure 3. *Chromatographic profiles of the distilled fractions (F1 and F2) from the bio-oil obtained by vacuum pyrolysis of olive oil, at 420°C, during 30 min (test T1).*

The fraction 1 of the bio-oil obtained from olive oil presents high concentrations of octane and nonane while the component with higher carbon number is heptadecane (C17) with only minor amounts of octadecane (C18). This behavior is consistent with the typical composition of olive oil, commonly dominated by oleic acid. This fatty acid has 18 carbons and by decarboxylation (loss of CO_2), yields *heptadecene*; this unsaturated hydrocarbon can suffer cleavage in its double bond to produce two primary products with 8 and 9 carbon atoms, which during the cooling phase of the reactor can rearrange to yield stable neutral molecules with these carbon numbers, namely the more stable isomers: octane and nonane *(Figure 3).*
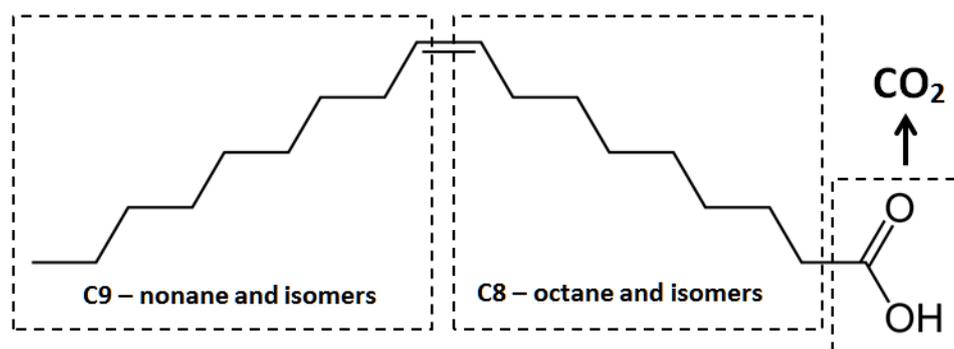
Image 6. *Schematic representation of the main pathways for the thermochemical decomposition of oleic acid*

The composition of fraction 2 also reflects these mechanisms, in particular the different concentrations of heptadecane and octadecane indicate that decarboxylation occurs in some extent. The presence of different hydrocarbons with carbon numbers from 9 to 17 is explained by reactions of recombination of the pyrolysis primary products with 9 carbons or less.

Besides oleic acid the major free fatty acids of olive oil are linoleic acid, linolenic acid and stearic acids (all with 18 carbons but different degrees of insaturation) and palmitic and palmitoleic acids with 16 carbons. All these fatty acids will also suffer reactions analogous to the ones described in *Figure 3* and in particular the decarboxylation of the 16 carbons fatty acids may explain the high concentration of pentadecane (C15) when compared to the other components *(Figure 3)*.

Finally, some minor amounts of hydrocarbons with 19 carbons and higher may either result from their presence, in low concentrations, in the olive oil or from the combination of higher molecular weight primary products.

The compounds that elute between two consecutive alkanes are isomers or related compounds with similar molecular weight that are formed by other reactions of recombination and isomerization.

When performing pyrolysis under vacuum conditions or with an inert gas atmosphere the carbon-carbon bonds will be cleaved but there is not a source of hydrogen atoms to complete the four bonds required by carbon atoms in sp3 hybridization. Therefore, the pyrolysis primary products tend to form double bonds and/or cyclic structures in order to yield neutral molecules. That is the main reason for the presence of a relatively high content of aromatic compounds in the pyrolysis oils, responsible for their pungent odor and high toxicity.

The relative concentrations of these different final products depend on their relative thermodynamic stability but also on kinetic factors since those recombination reactions are also influenced by the velocity of cooling of the pyrolytic vapors. The chromatographic profiles of the two distilled fractions from the bio-oil produced with olive husk oil at 420 °C and 30 min are presented in *Figure 4*.
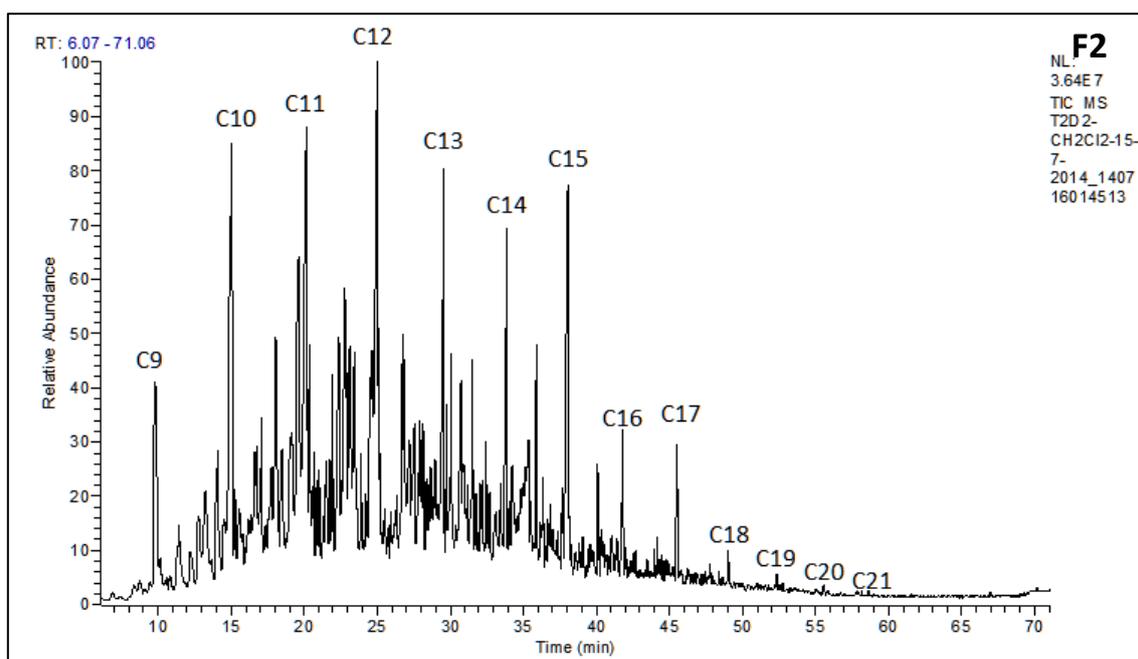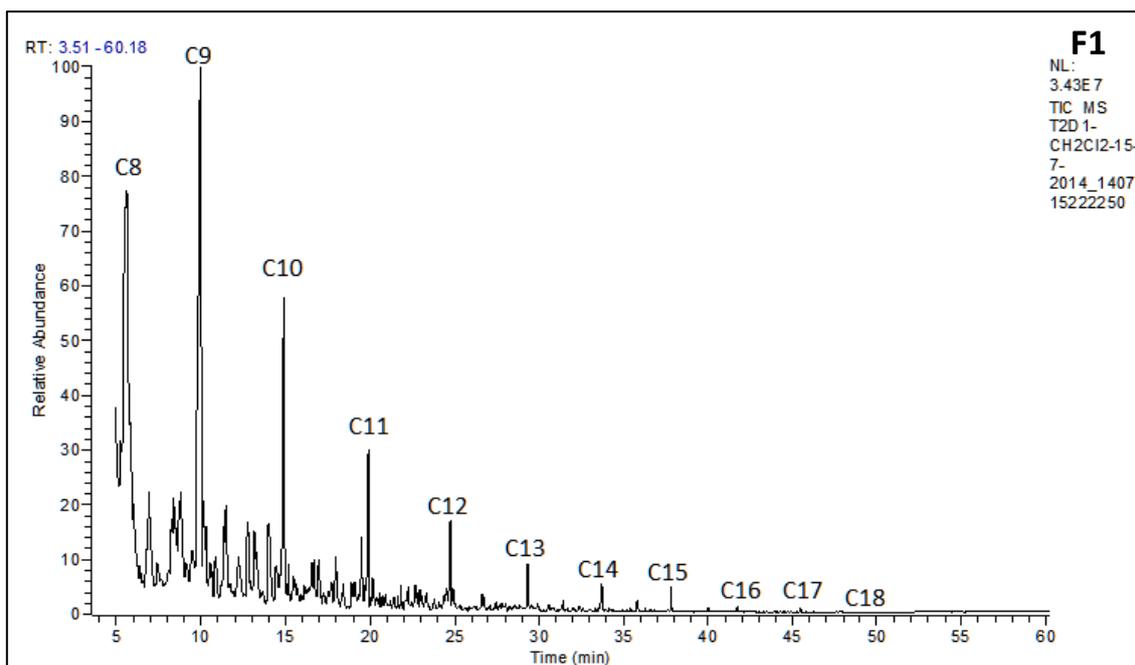
Figure 4. *Chromatographic profiles of the distilled fractions (F1 and F2) from the bio-oil obtained by vacuum pyrolysis of olive husk oil, at 420°C, during 30 min (test T2).*

The profiles presented in *Figure 4* are similar to the ones of *Figure 3* which is expectable since the raw materials are both vegetable oils produced from the olive fruit, except for the higher content of free fatty acids usually present in the olive husk oil. This higher acidity will facilitate the thermal degradation of the oils because it

means that a higher fraction of the triglycerides are already partially decomposed. As a consequence, a higher proportion of lighter hydrocarbons are found in this bio-oil and it also presents lower concentrations of hexadecane (C16) and heptadecane (C17).The chromatographic profiles of the two distilled fractions from the bio-oil produced with animal fat, at 420 °C and 30 min are presented in *Figure 5.*
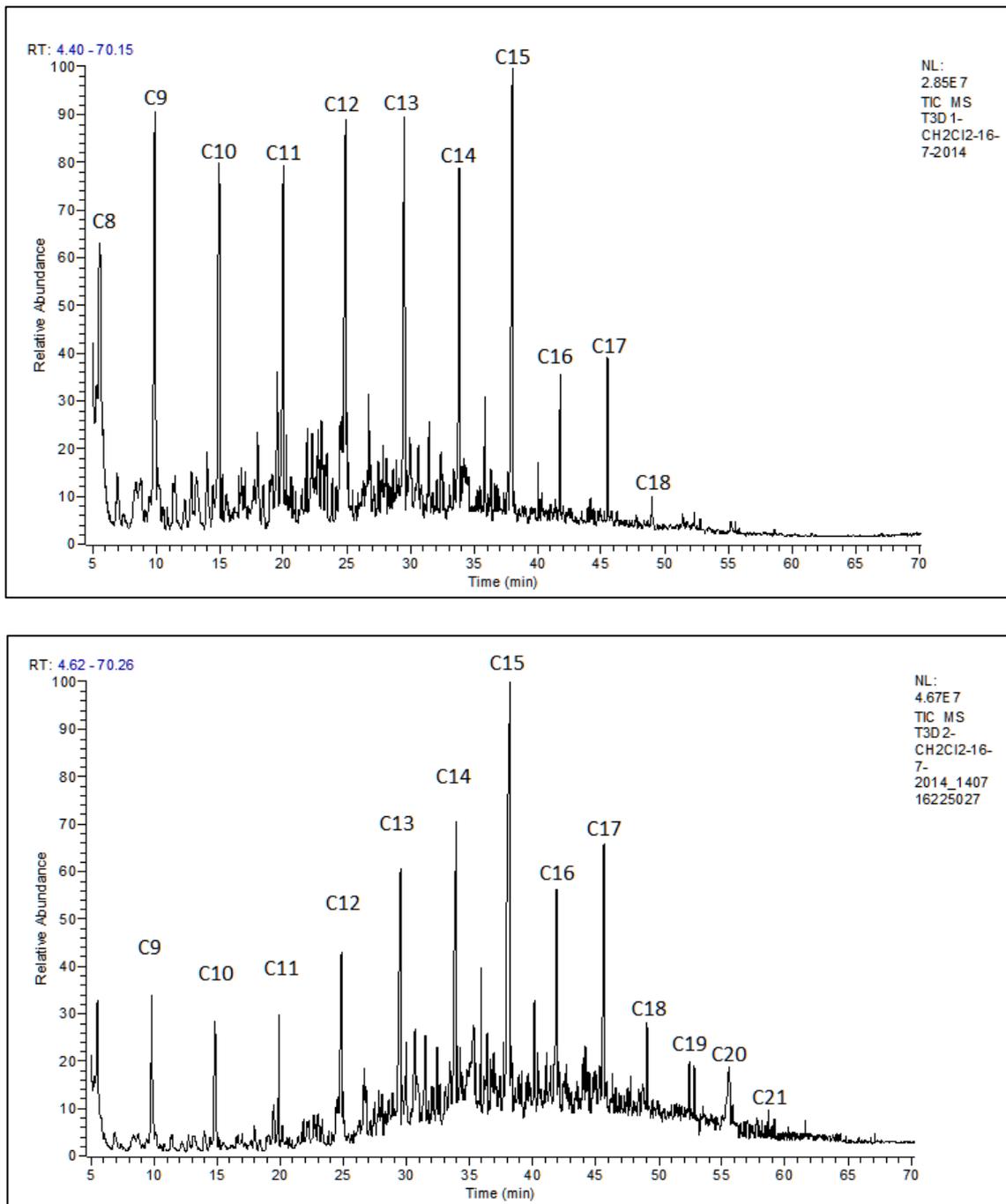
Figure 5. *Chromatographic profiles of the distilled fractions (F1 and F2) from the bio-oil obtained by vacuum pyrolysis of animal fat (17%), at 420 °C, during 30 min (test T3).*

The animal fats are characterized by higher concentrations of saturated fatty acids such as stearic acid (C18) and palmitic (C16) when compared with the vegetable oils. The free fatty acids will tend to react differently under pyrolysis conditions because all carbon-carbon bonds in the side chain are equivalent. Thus, besides the decarboxylation or decarbonilation reactions, further decomposition of the hydrocarbon chain can occur in any other bond so the probability of formation of products with different carbon numbers is equivalent.
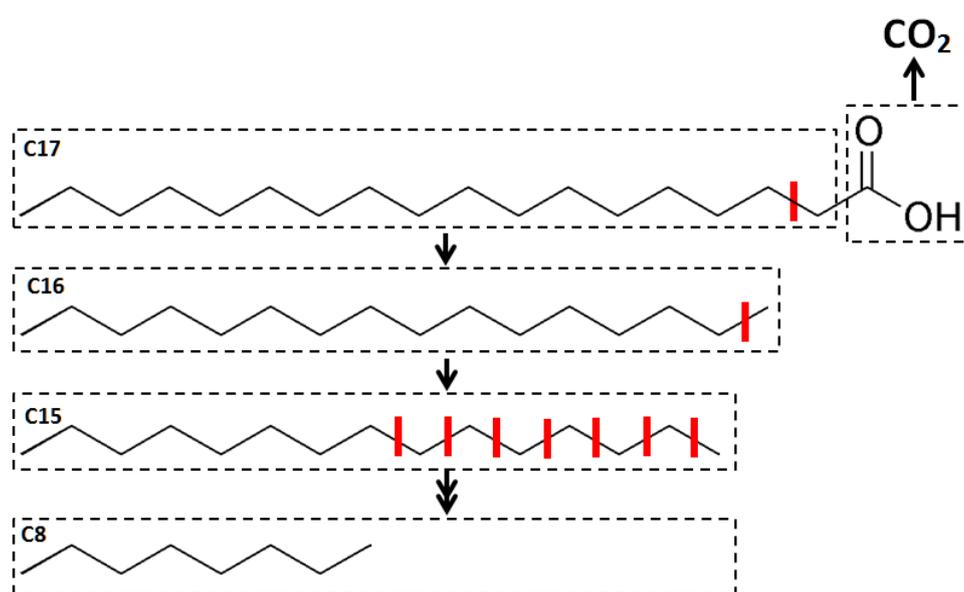
Image 7. *Schematic representation of the sequential decomposition of a saturated fatty acid after decarboxylation under pyrolytic conditions.*

This different thermochemical degradation pathways result in higher concentrations of hydrocarbons with higher carbon numbers namely equivalent concentrations of the hydrocarbons from C9 to C15 in fraction 1. The relative concentrations of heptadecane (C17) and hexadecane (C16) are also high in both fractions when compared with the concentrations of those hydrocarbons in bio-oils produced with vegetable oils.

The carbon number distribution of the bio-oil components was evaluated by making the assumption that the compounds eluted between two adjacent linear hydrocarbons have carbon numbers identical to those hydrocarbons; thus their individual relative concentrations were grouped, and represented as a function of the corresponding carbon numbers *(Figure 6)*.

Since one of the main applications of pyrolysis bio-oils or hydrogenated vegetable oils is their use as biofuels in internal combustion engines this analysis is appropriate for the evaluation of their fuel potential that is strongly dependent on the distribution of carbon numbers of their components.
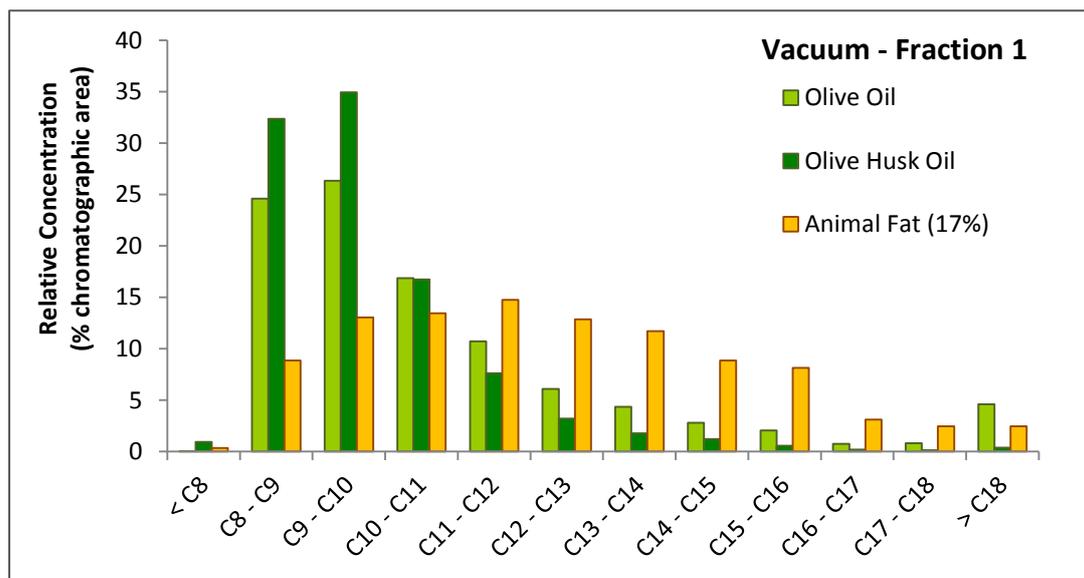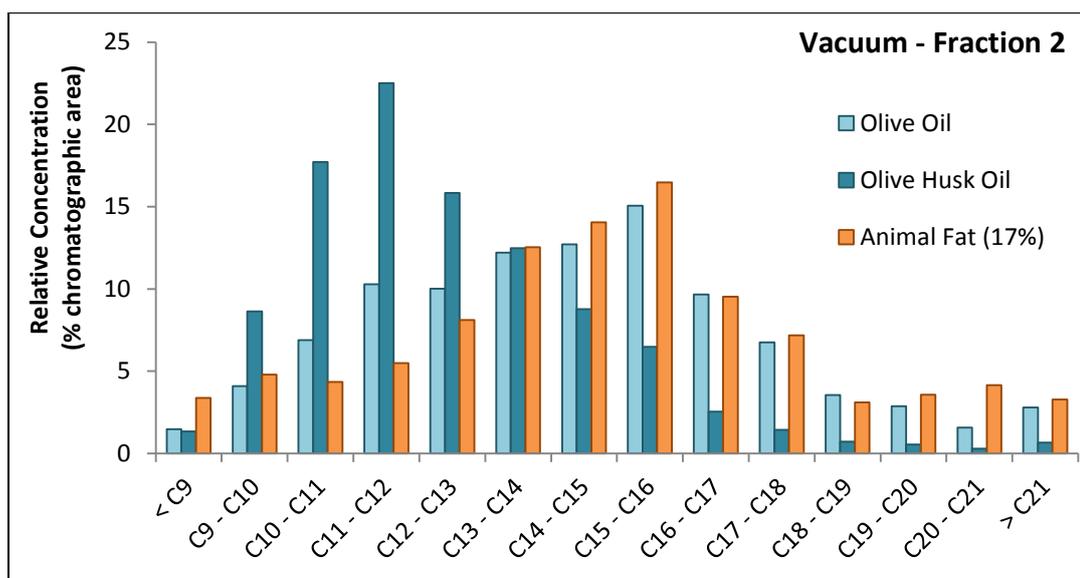
Figure 6. *Carbon number distribution of the distilled bio-oil components, from the pyrolysis of the various raw materials, under a vacuum atmosphere.*

4.3 Pyrolysis of oils and fats under a Nitrogen atmosphere

Raw Materials	Initial Pressure (bar)	Pyrolysis Yields (% w/w)			Distillation Yields (% w/w)		
		Gases	**Liquids**	**Solids**	**F1**	**F2**	**F1+F2**
Olive Oil	3	19.7	80.3	0.0	39.3	48.2	87.4
Olive Husk Oil	3	18.1	81.9	0.0	12.7	73.1	85.9
Animal Fat (17%)	2.4	26.0	74.0	0.0	18.3	58.0	76.3

Table 8. *Mass yields of pyrolysis of oils and fats, at 420 ^{o}C, during 10 min under a nitrogen atmosphere and distillation of the corresponding bio-oils*
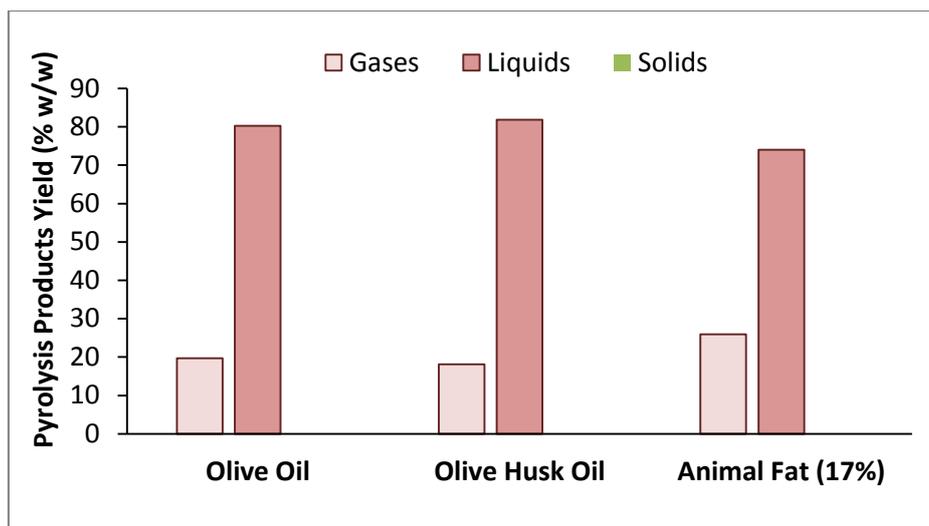
Figure 7. *Pyrolysis of oils and fats at 420 ℃, 10 min under a nitrogen atmosphere: product yields for gases, liquids and solids.*
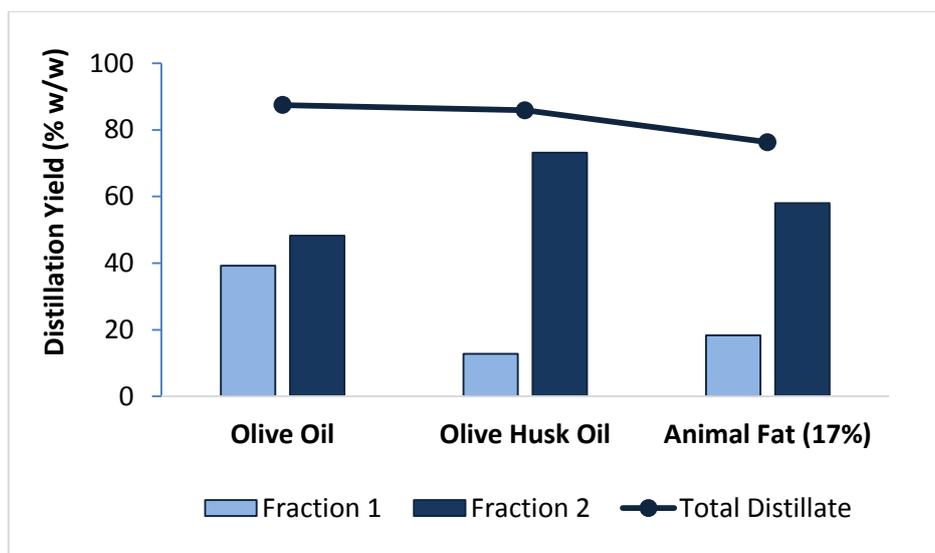
Figure 8. *Distillation of the pyrolysis bio-oils obtained at 420 ℃, during 10 min under a nitrogen atmosphere.*

4.3.1 Composition of the Distilled Fractions
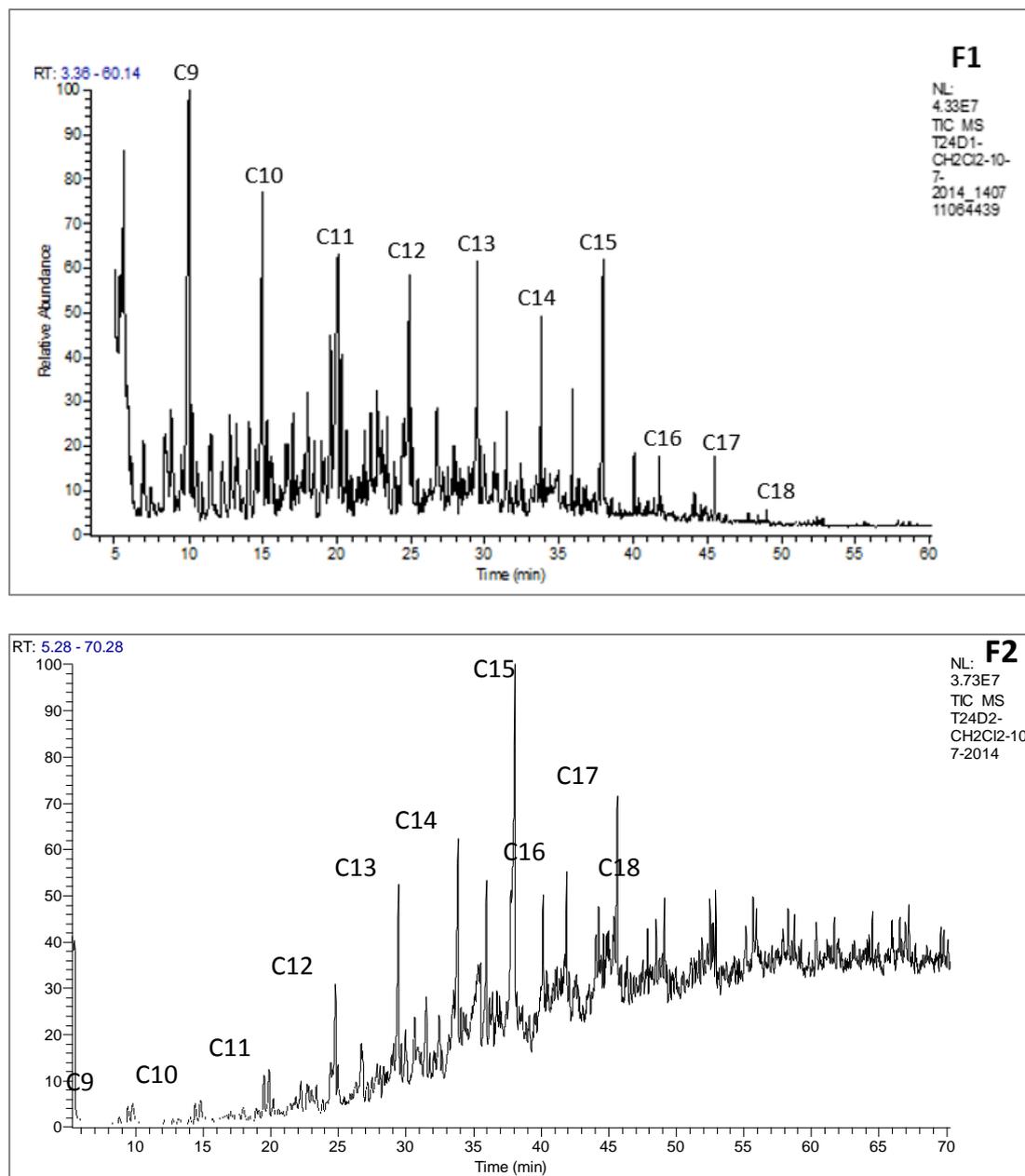
Figure 9. *Chromatographic profiles of the distilled fractions (F1, F2) from the pyrolysis bio-oil obtained from olive oil, at 420°C, during 10 min, under a nitrogen atmosphere (T4).*

The fraction 1 of the bio-oil obtained from olive oil presents high concentration of nonane in this case and the component with higher carbon number is heptadecane (C17), whereas we can note small amounts of octadecane (C18).

Moreover, in this chromatographic profile, we can observe that there are relevantly similar amounts of decane (C10), undecane (C11), dodecane (C12), tridecane (C13), tetradecane (C14) and pentadecane (C15).

The composition of fraction 2 is quite different though. It is clearly noted that there is a significant decrease in the concentration from nonane (C9) until dodecane (C12) and a progressive increase in the number of carbons, *as figure 9-F2* shows. The concentration of the roots from tetradecane (C14) to octadecane (C18) is significantly increased and later on, stabilized.
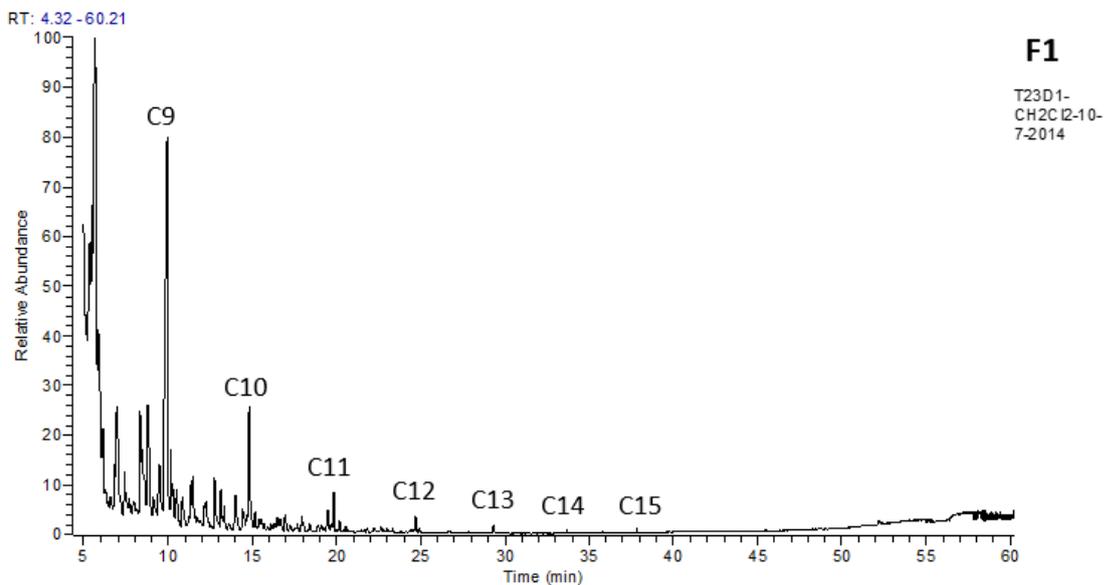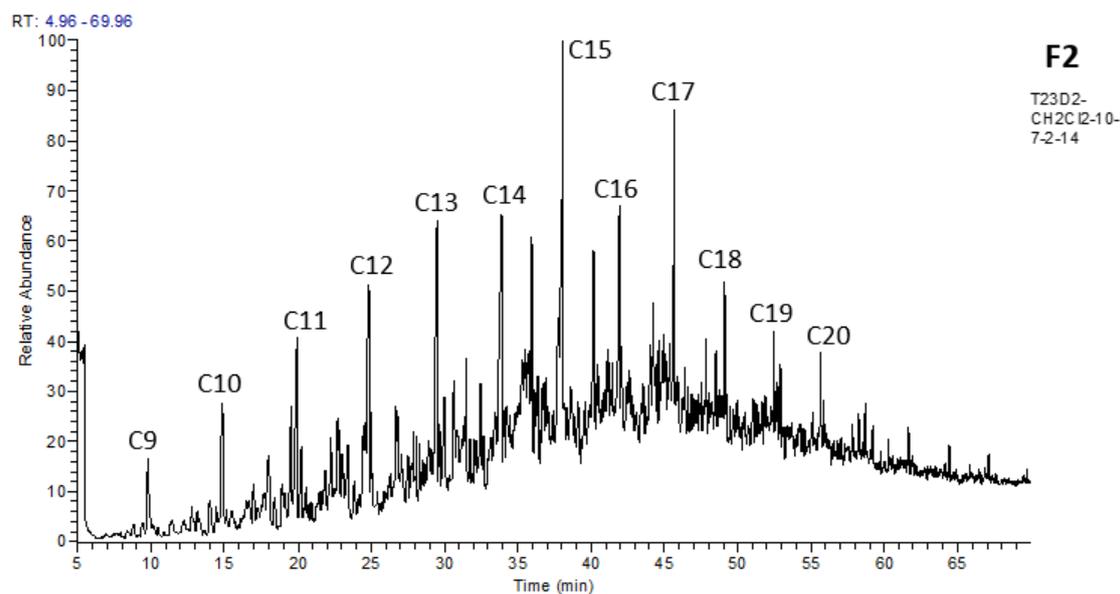
Figure 10. *Chromatographic profiles of the distilled fractions (F1, F2) from the pyrolysis bio-oil obtained from olive husk oil, at 420°C, during 10 min, under a nitrogen atmosphere (T5).*

The profiles presented in *Figure 10 – F1* are quite similar to the ones of *Figure 11* what is expectable since the raw materials are both vegetable oils produced from the olive fruit. The high amount of fatty acids usually present in the olive husk oil can be still clearly observed. What can be also observed is that the decrease of carbon concentration in fraction one is quite steep; meaning that there is a quite big concentration of nonane (C9), but after this, the concentration of decane (C10) is quite lower and then of undecane (C11) to pentadecane (C15) almost nonexistent.

In the composition of fraction 2 it is clearly noted that there is a significant decrease in the concentration of carbons from nonane (C9) until pentadecane (C15) and a progressive increase in the number of the rest carbons, from hexadecane (C16) and onwards, as *figure 10-F2* shows. It is important to note that the carbons after eicosane (C20) are not reaching zero.
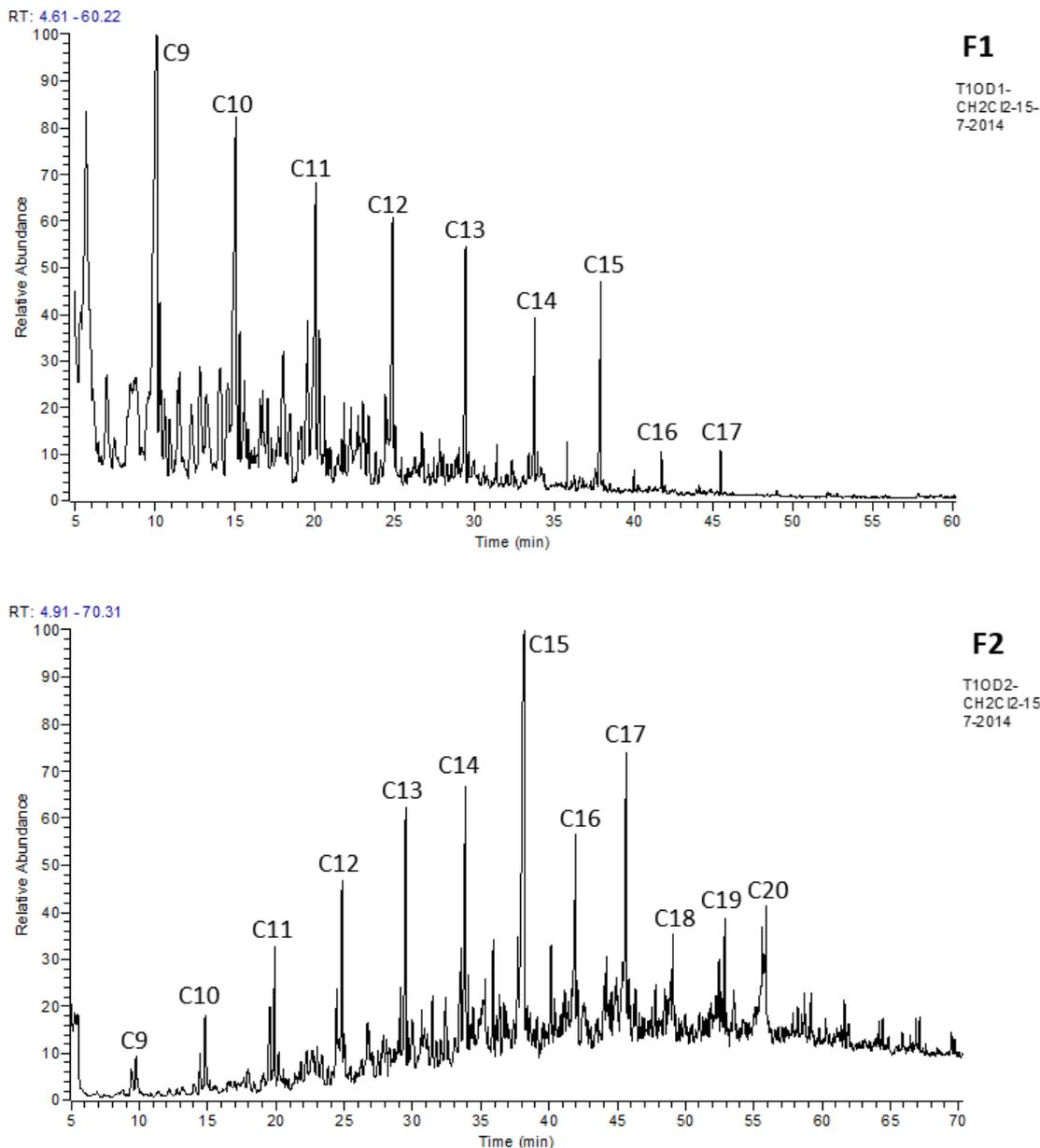
Figure 11. *Chromatographic profiles of the distilled fractions (F1, F2) from the pyrolysis bio-oil obtained from animal fat (17%), at 420°C, during 10 min, under a nitrogen atmosphere (T6).*

In this chromatographic profile we can observe that the concentration of the carbon numbers is quite high. There are big concentrations of nonane (C9), decane (C10), undecane (C11), dodecane (C12). Moreover, small concentrations of hexadecane (C16) and heptadecane (C17) are observed, which can be a result of occuring decarboxylation of saturated fatty acids existing in animal fats, under

pyrolytic conditions. This profile of the first fraction of animal fats has not changed much now, reacting with nitrogen, in comparison to the one under vacuum conditions.

Minor differences to the profile under vacuum conditions can be observed also in fraction 2. A small decrease in the concentrations of nonane (C9) and decane (C10) are noted as well as a small increase in those of octadecane (C18), nanodecane (C19) and eicosane (C20). The rest of carbons' concentrations remain, generally, quite steady in this profile.
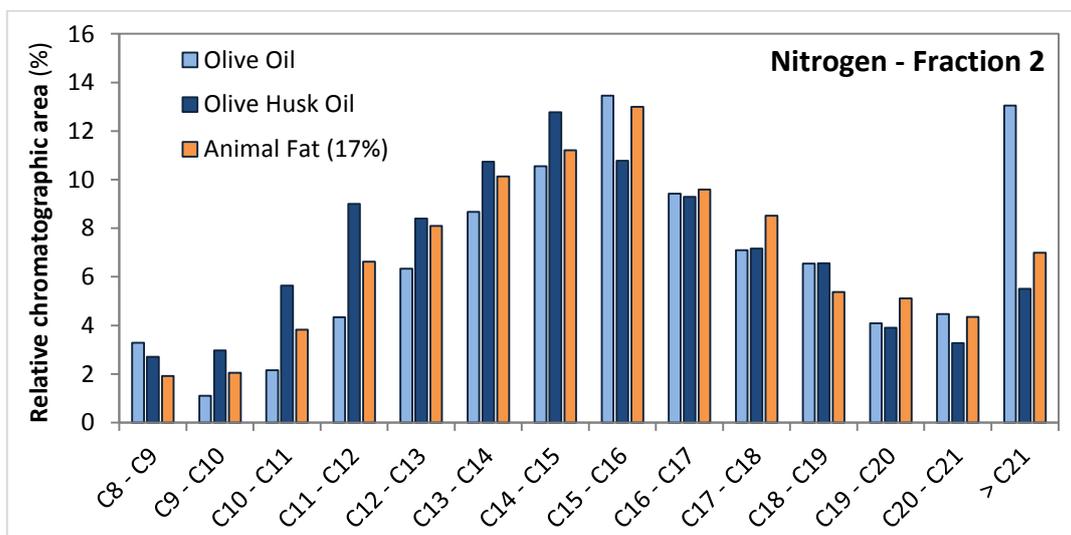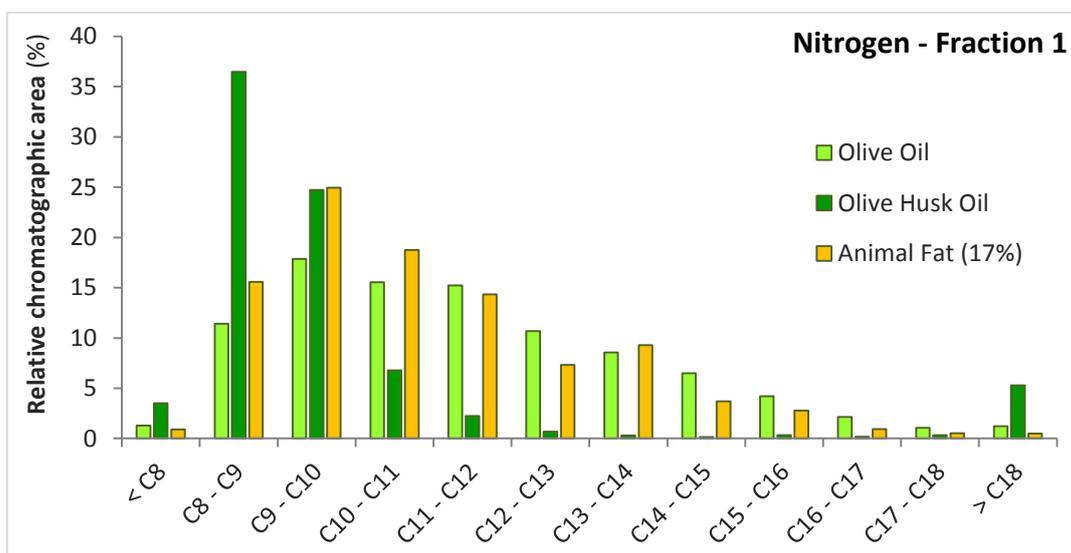
*Figure 12.*Carbon number distribution of the distilled bio-oil components, from the pyrolysis of the various raw materials, under a nitrogen atmosphere.

4.4 Pyrolysis of oils and fats under a Methane atmosphere

Raw Materials	Initial Pressure (bar)	Reaction Time (min)	Pyrolysis Yields (% w/w)			Distillation Yields (% w/w)		
			Gases	Liquids	Solids	F1	F2	F1+F2
Olive Oil	3	10	19.2	80.8	0.0	16.9	57.2	74.1
Olive Husk Oil	3	10	14.1	85.9	0.0	29.2	48.5	77.7
Animal Fat (17%)	3	10	18.7	81.3	0.0	18.1	40.4	58.5

Table 9. *Mass yields of pyrolysis of oils and fats, at 420 ^{o}C, during 10 min under a methane atmosphere and distillation of the corresponding bio-oils.*
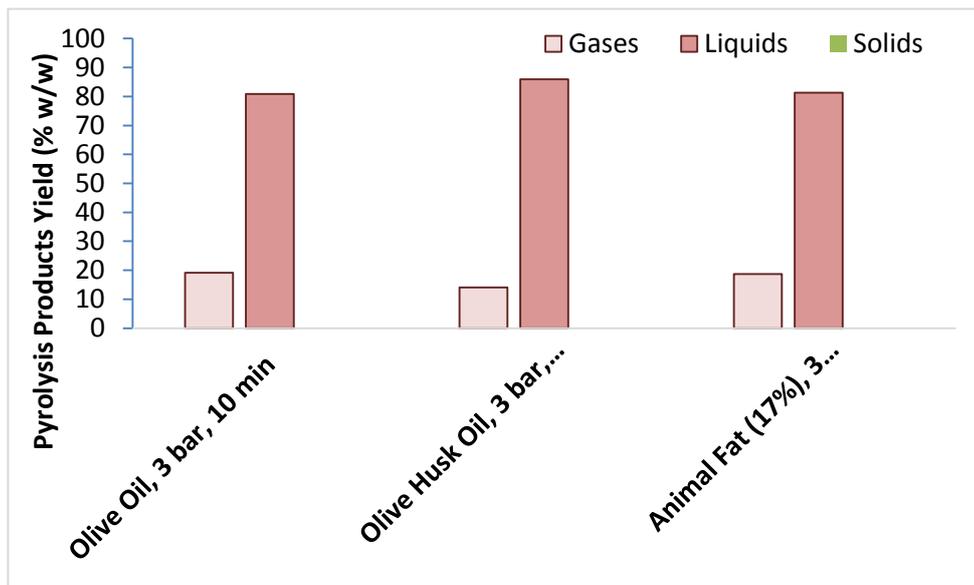
**Figure 13.** *Pyrolysis yields obtained at 420 °C, under a methane atmosphere*
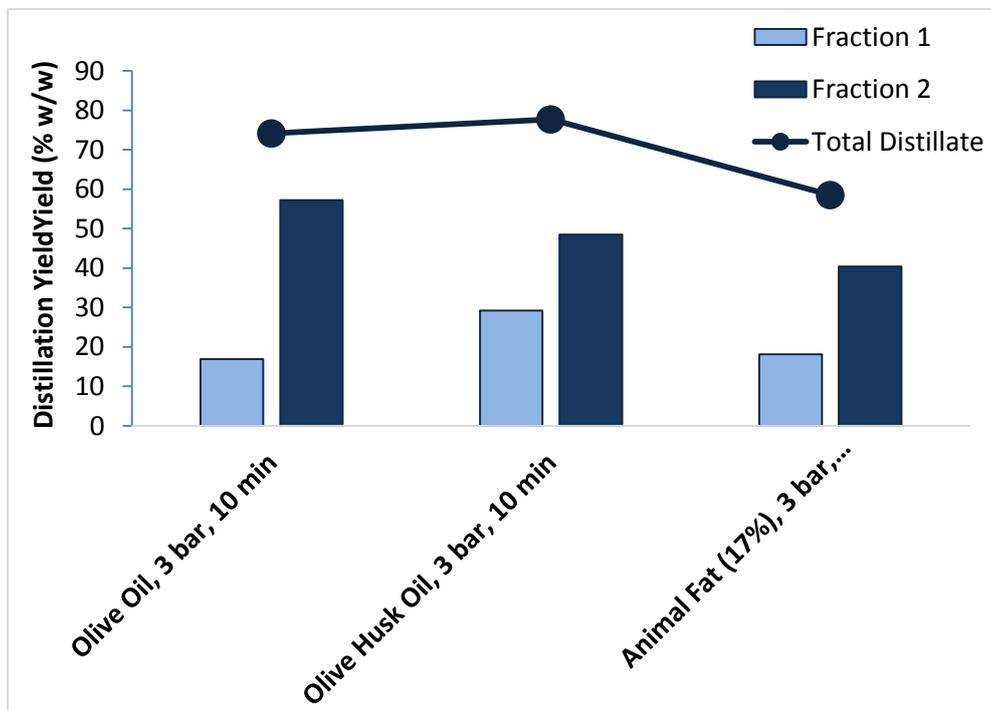
Figure 14. *Distillation of the pyrolysis bio-oils obtained at 420 °C, under a methane atmosphere*
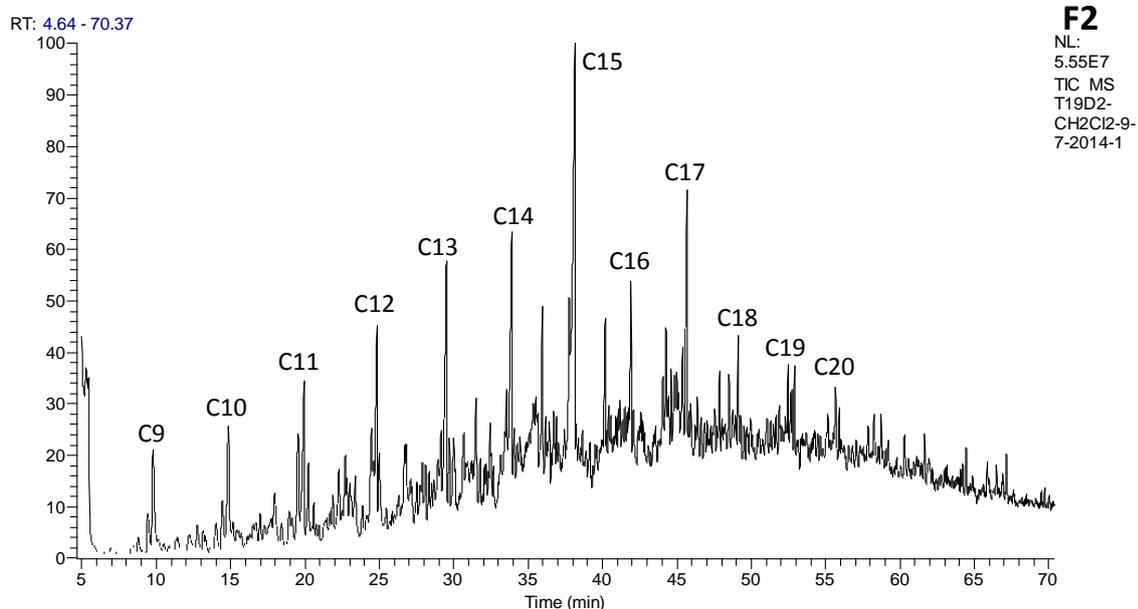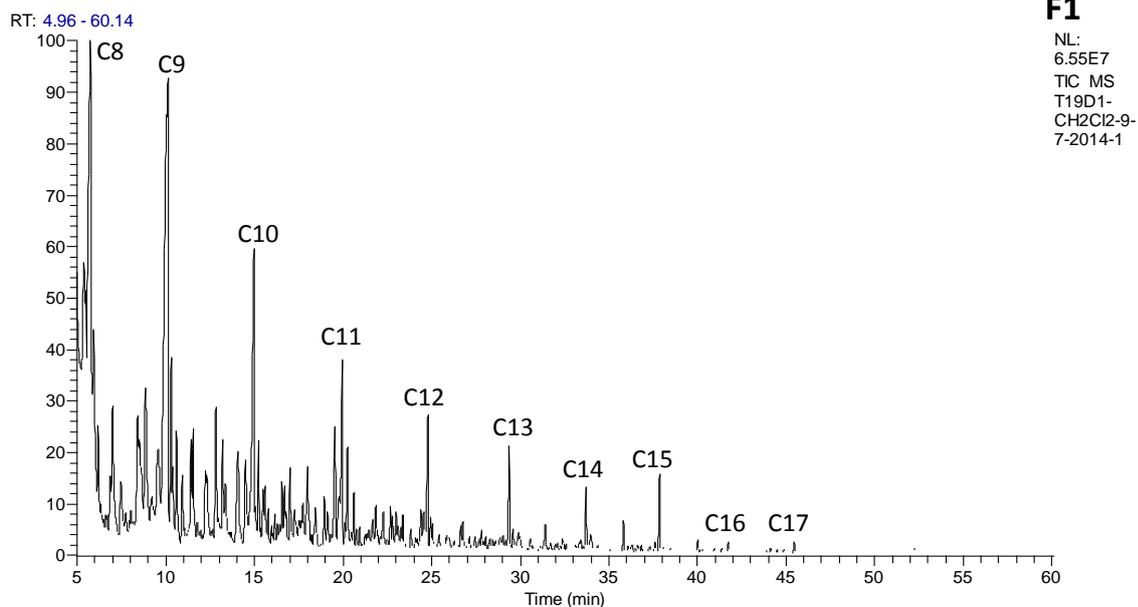
Figure 15. *Chromatographic profiles of the distilled fractions (F1, F2) from the pyrolysis bio-oil obtained with olive oil, at 420℃, during 10 min, under a methane atmosphere (T7).*

The composition of the chromatographic profile of animal fats pyrolysed under methane atmosphere is quite similar to the two previous ones, conducted under vacuum and nitrogen atmospheres. Thus, the carbon composition diagram involves high concentrations of nonane (C9) and decane (C10) as well as a radial decrease of the carbons' concentrations.

The same applies for the second fraction as well, an increase in the concentrations of carbons is observed, more specifically from nonane (C9) to pentadecane (C15) combined with a small decrease of the further carbon concentrations; those of hexadecane (C16) to eicosane (C20).
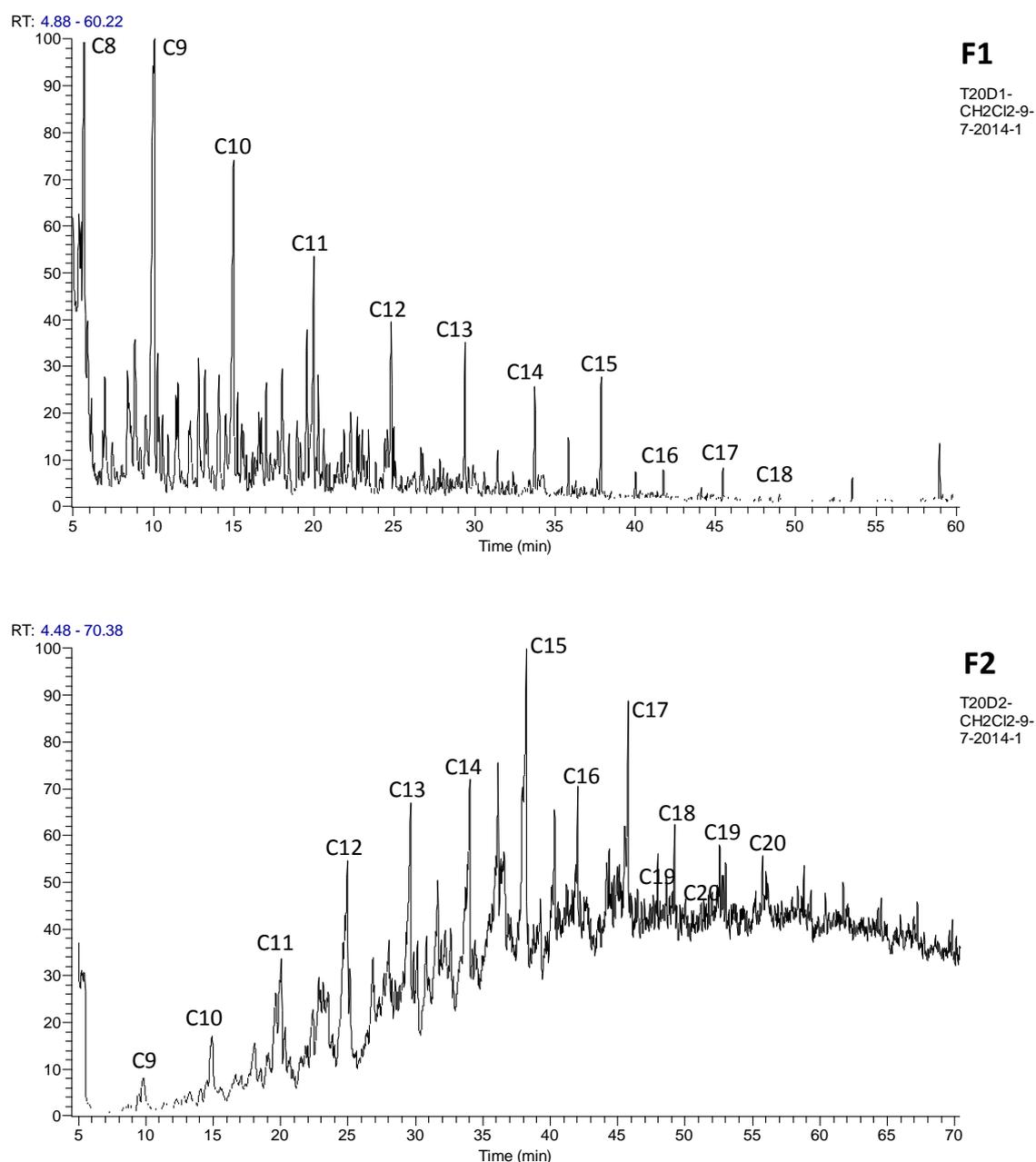

Figure 16. *Chromatographic profiles of the distilled fractions (F1, F2) from the pyrolysis bio-oil obtained with olive husk oil, at 420°C, during 10 min, under a methane atmosphere (T8).*

Regarding the light fraction of this chromatographic profile, *fraction 1-F1*, it is observed that has no important variations, in comparison with the rest samples of olive husk oil, under vacuum and nitrogen atmosphere. What is quite interesting to be noted, is the behavior of the heavier fraction, *fraction 2-F2*. Starting from really low carbon concentrations (of nonane (C9)), there is a steady increase in the composition of the sample in carbons, reaching the top peak of pentadecane (C15).

F2

T16D2-
CH2Cl2-16-
7-2-14
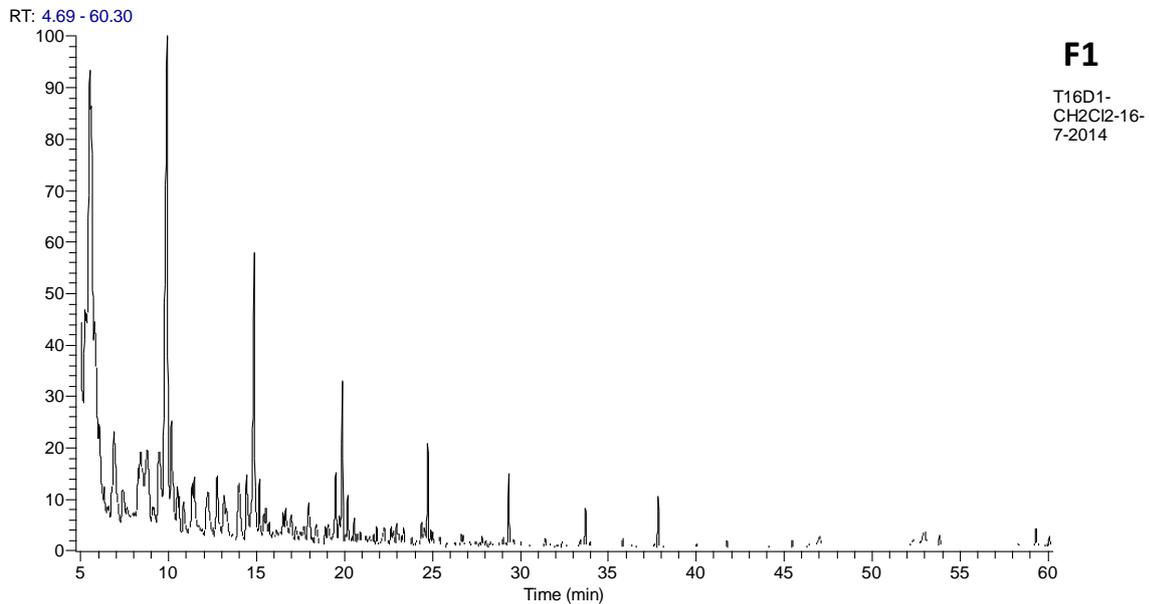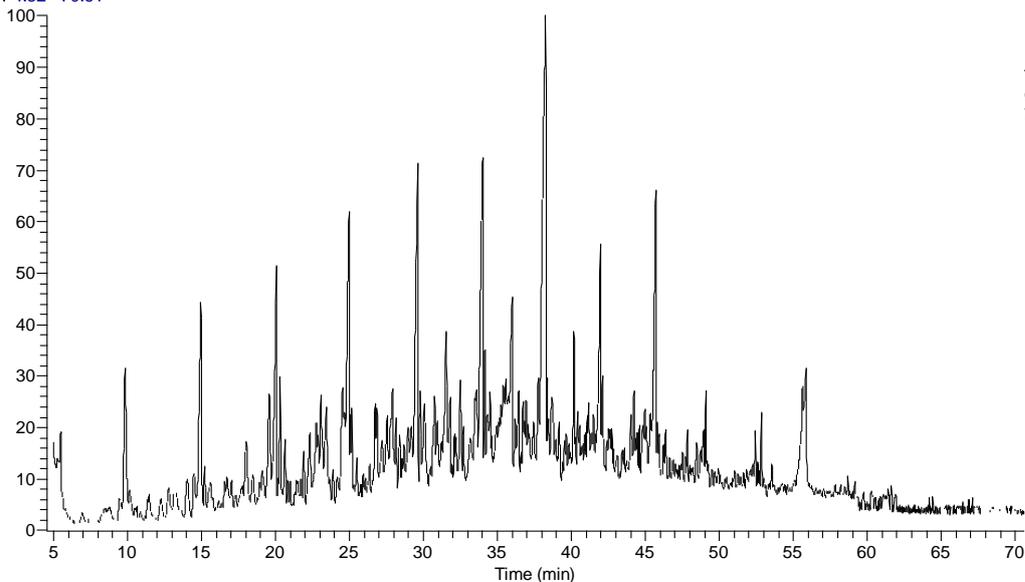
Figure 17. Chromatographic profiles of the distilled fractions (F1, F2) from the pyrolysis bio-oil obtained with animal fat (17%), at 420°C, during 10 min, under a methane atmosphere (T9).
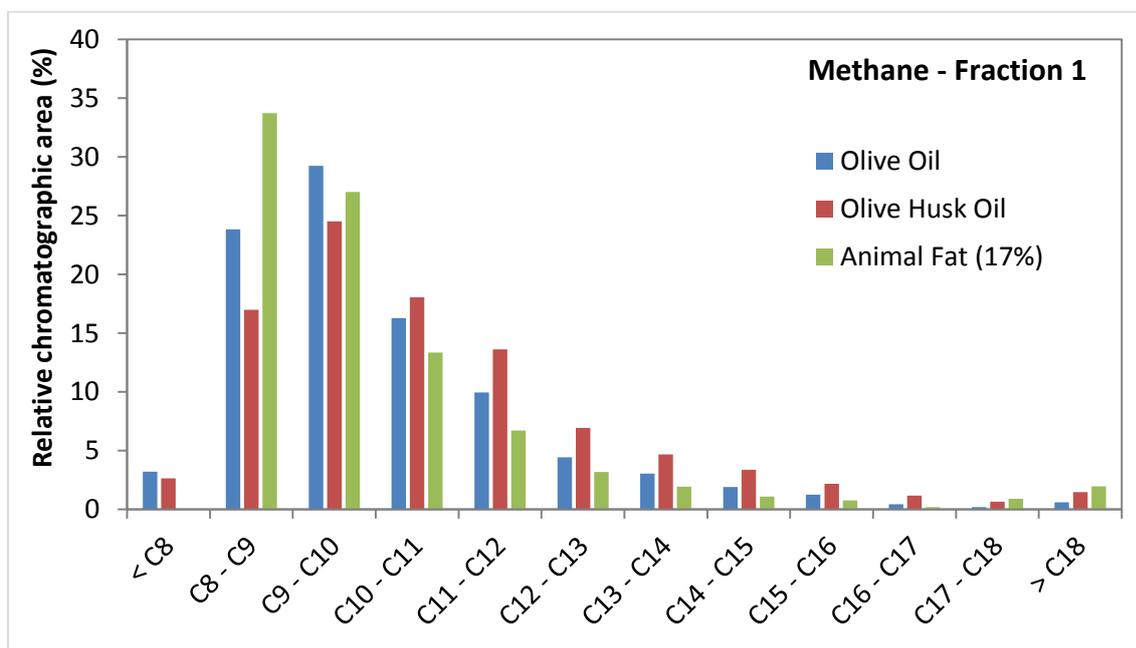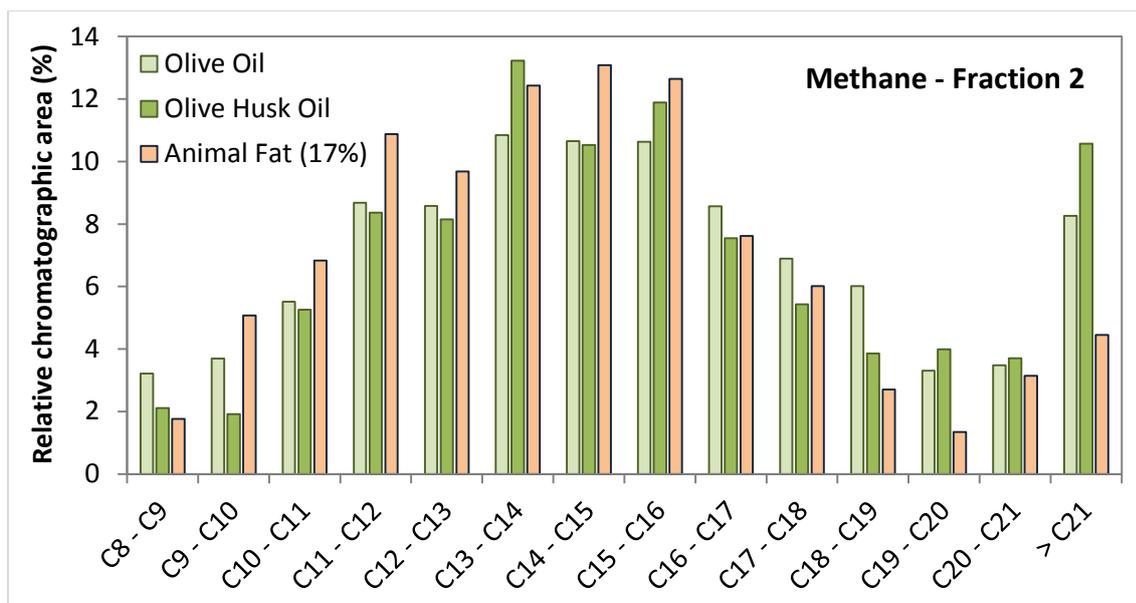
Figure 18. *Carbon number distribution of the distilled bio-oil components, from the pyrolysis of the various raw materials, under a methane atmosphere.*

5. DISCUSSION

5.1 Comparison of the pyrolysis products obtained under different atmospheres

Initially, in order for all the experiments conducted in the laboratory to be discussed, they have to be demonstrated and gathered. They are presented in *Table 10.*

ATMOSPHERE						
Vacuum						
Raw material		**Carbon type**	**Maximum Carbon relative concentration (%)**	**Distillation yield (F1)**	**Pressure (bar)**	**Time (min)** / **Temperature (^{o}C)**
Olive oil	T1	C9-C10	26.31	33.7	0	30 / 420
Olive Husk Oil	T2	C9-C10	34.92	17.7	0	30 / 420
Animal fat (17%)	T3	C11-C12	17.75	43.9	0	30 / 420
Nitrogen						
Raw material		**Carbon type**	**Maximum Carbon relative concentration (%)**	**Distillation yield (F1)**	**Pressure (bar)**	**Time (min)** / **Temperature (^{o}C)**
Olive oil	T4	C9-C10	17.87	39.3	3	10 / 420
Olive Husk Oil	T5	C8-C9	36.48	12.7	3	10 / 420
Animal fat (17%)	T6	C9-C10	24.93	18.3	3	10 / 420
Methane						
Raw material		**Carbon type**	**Maximum Carbon relative concentration (%)**	**Distillation yield (F1)**	**Pressure (bar)**	**Time (min)** / **Temperature (^{o}C)**
Olive oil	T7	C9-C10	29.26	16.9	3	10 / 420
Olive Husk Oil	T8	C9-C10	24.52	29.2	3	10 / 420
Animal fat (17%)	T9	C8-C9	33.74	18.1	3	10 / 420

**Table 10.** *Experiments carried out and experimental conditions*

Fraction 1:
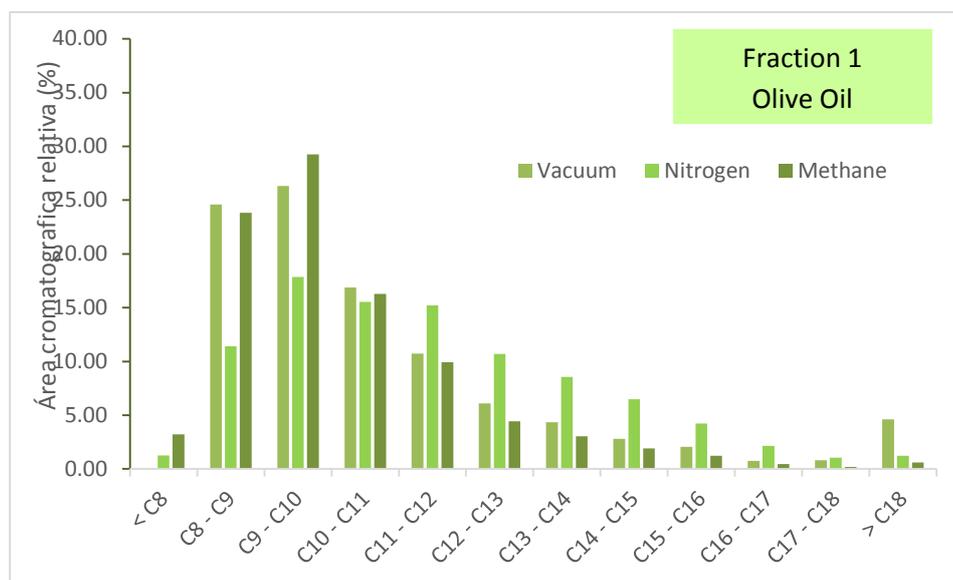
Figure 19. *Carbon number distribution of the distilled bio-oil components (Fraction 1), from the pyrolysis of olive oil at 3 bar, during 10 min, under different atmospheres.*
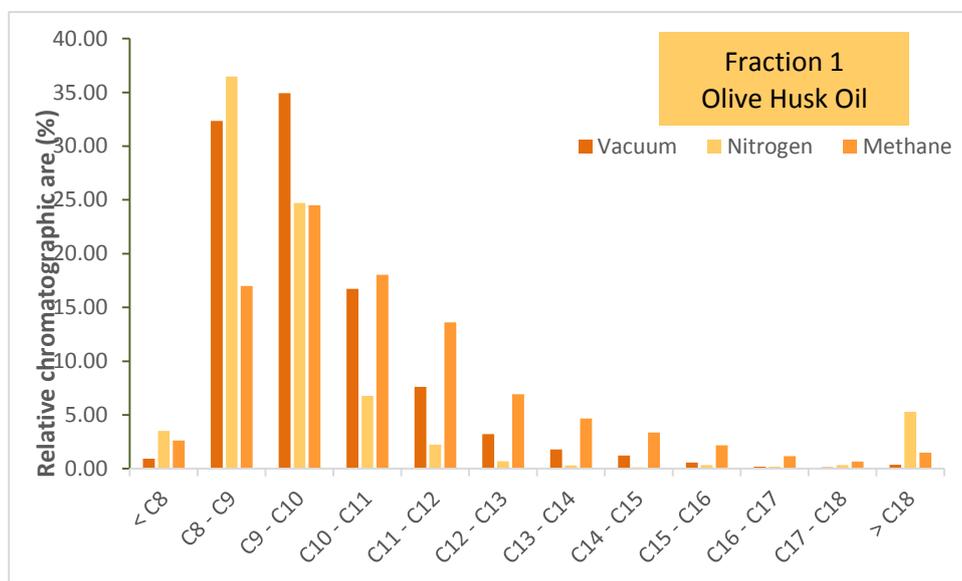

Figure 20. *Carbon number distribution of the distilled bio-oil components, from the pyrolysis of olive husk oil at 3 bar, during 10 min, under different atmospheres.*
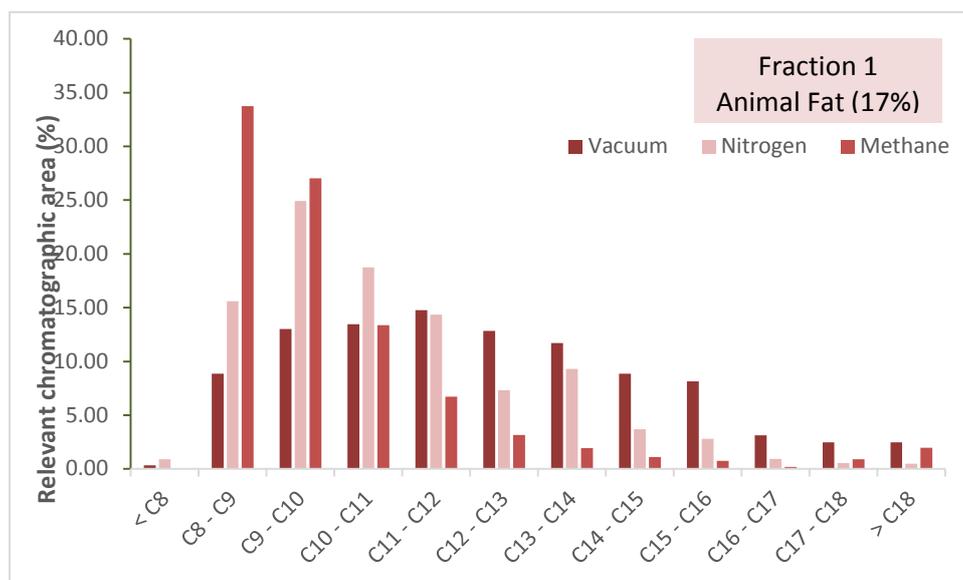
Figure 21. *Carbon number distribution of the distilled bio-oil components, from the pyrolysis of animal fat (17%) at 3 bar, during 10 min, under different atmospheres.*

Very similar fatty acid profiles are noted for the fraction 1 of the oils tested during the experiments in almost every condition. More specifically, for the 1st fraction of *olive oil*, it is noted that the fatty acids with higher concentrations are the ones from C8 to C12, especially for vacuum and methane atmospheres. Their concentrations approach 25% for vacuum and 30% for methane atmosphere. This olive oil under nitrogen atmosphere, however, does not reach very high fatty acid concentrations, since it reaches only up to 18%, for acids from C9 to C10.

Regarding the *olive husk oil* profile now, it can be easily observed that it is very similar to the one of olive oil, presenting higher fatty acid concentrations of C8 to C11. However, in this case the atmosphere which is not quite suitable for the oil is the methane atmosphere, since it is noted that the highest percentage reached is that of 25%, in comparison to both vacuum and nitrogen which in this case reach the percentage of 37% and 35%, respectively for a carbon acid range from C8 to C10 .

Noteworthy is the following figure, the one of *animal fats (17% acidity),* since it presents a slightly different fatty acid profile. It is noted that presents the highest fatty acid concentrations under a methane atmosphere, reaching up to 35% for C8 and C9 acids, while gradually these concentrations are getting lower as noted in almost all light fractions of distillations. On the other hand, vacuum atmosphere proves to be not so efficient for the fat, since it accumulates small concentrations of fatty acids, reaching a maximum of 15% for acids from C11 and C12, whereas nitrogen is also in low levels, presenting a maximum concentration of 25%.

Hereby, the same figures as previously are presented, but in this case they are viewed under different atmospheres.
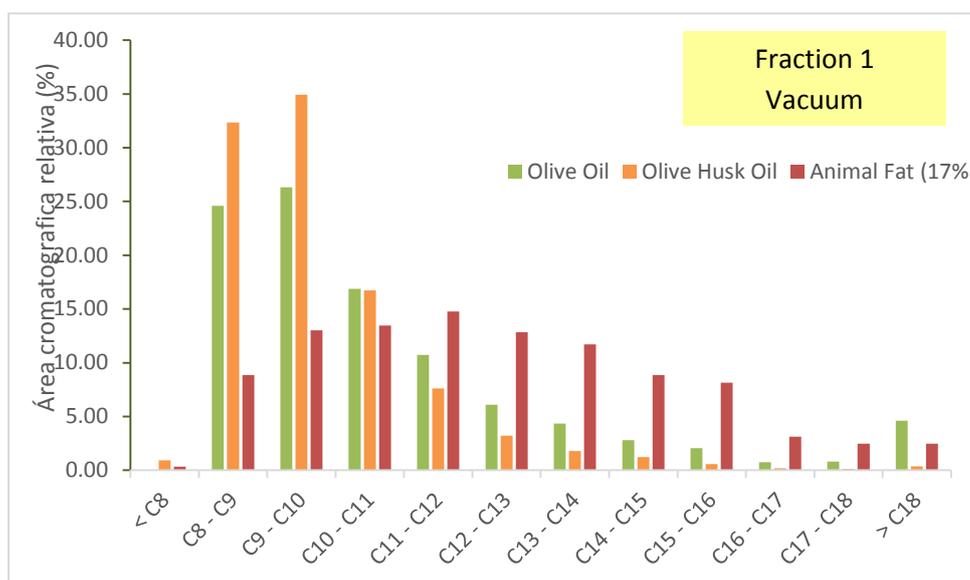
Figure 22. *Carbon number distribution of the distilled bio-oil components (Fraction 1), from the pyrolysis of all oils, at 0 bar, during 30 min, under vacuum atmosphere.*
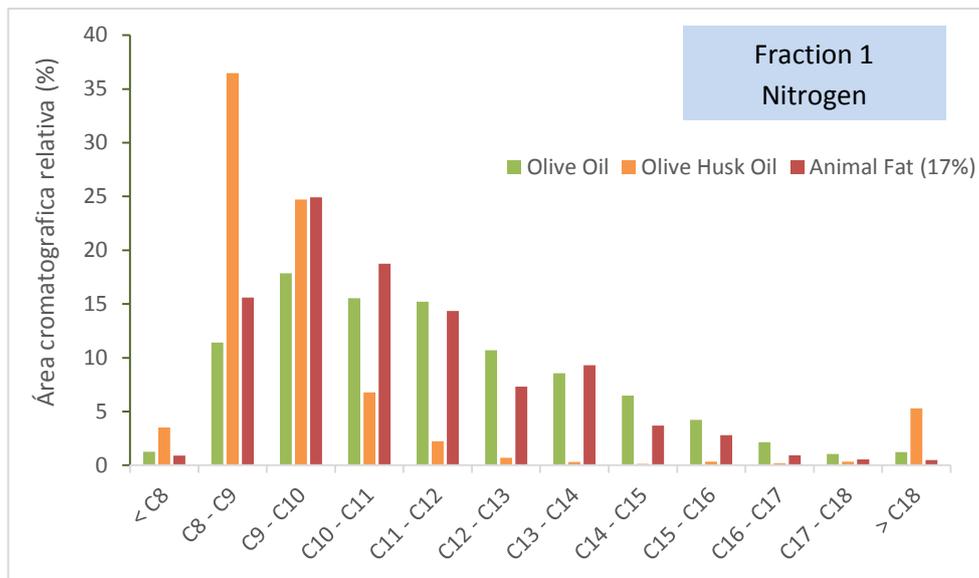
Figure 23. *Carbon number distribution of the distilled bio-oil components (Fraction 1), from the pyrolysis of all oils, at 3 bar, during 10 min, under nitrogen atmosphere.*
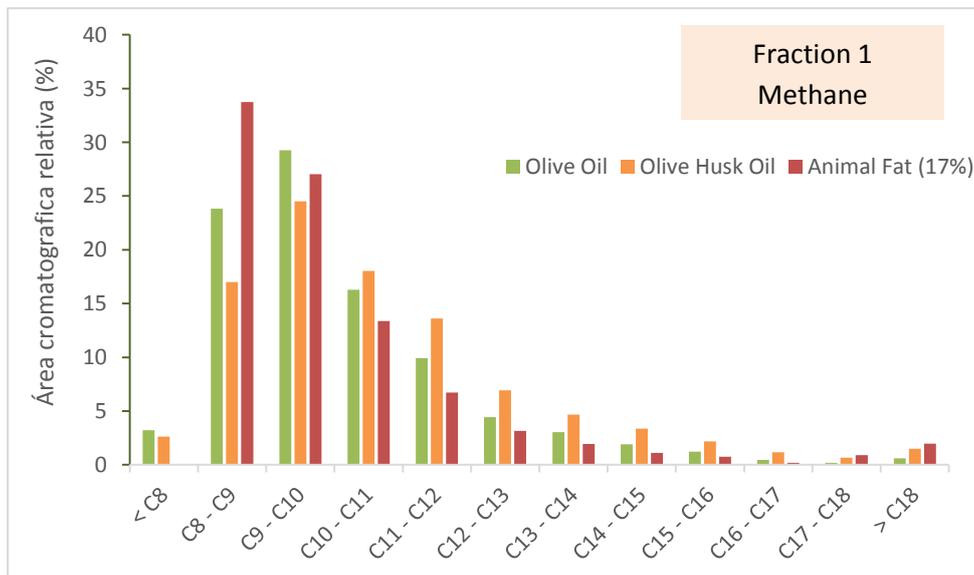

Figure 24. *Carbon number distribution of the distilled bio-oil components (Fraction 1), from the pyrolysis of all oils, at 3 bar, during 10 min, under methane atmosphere.*

Fraction 2:
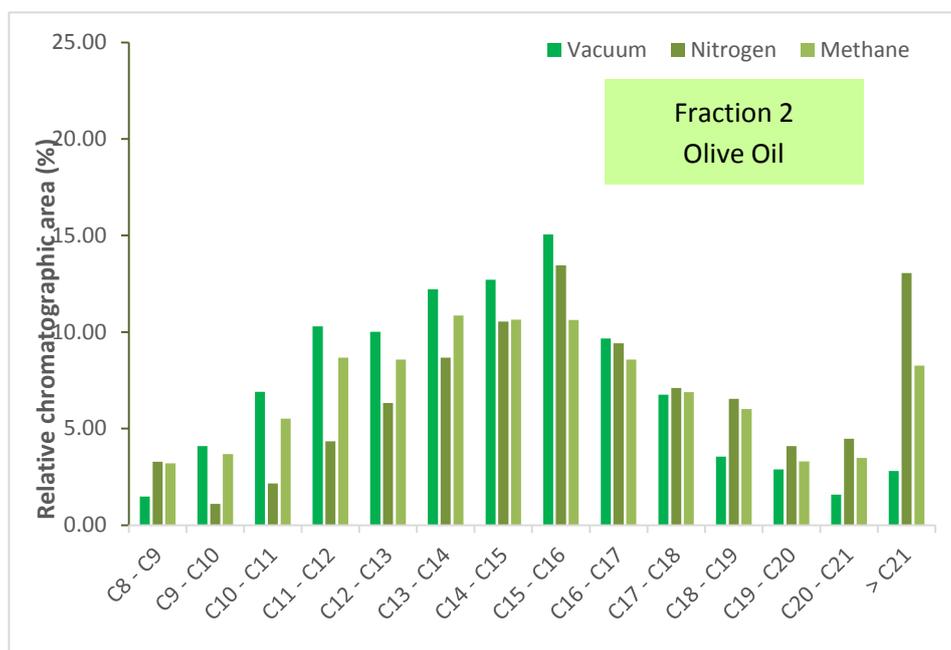
Figure 25. *Carbon number distribution of the distilled bio-oil components (Fraction 2), from the pyrolysis of olive oil at 3 bar, during 10 min, under different atmospheres*.
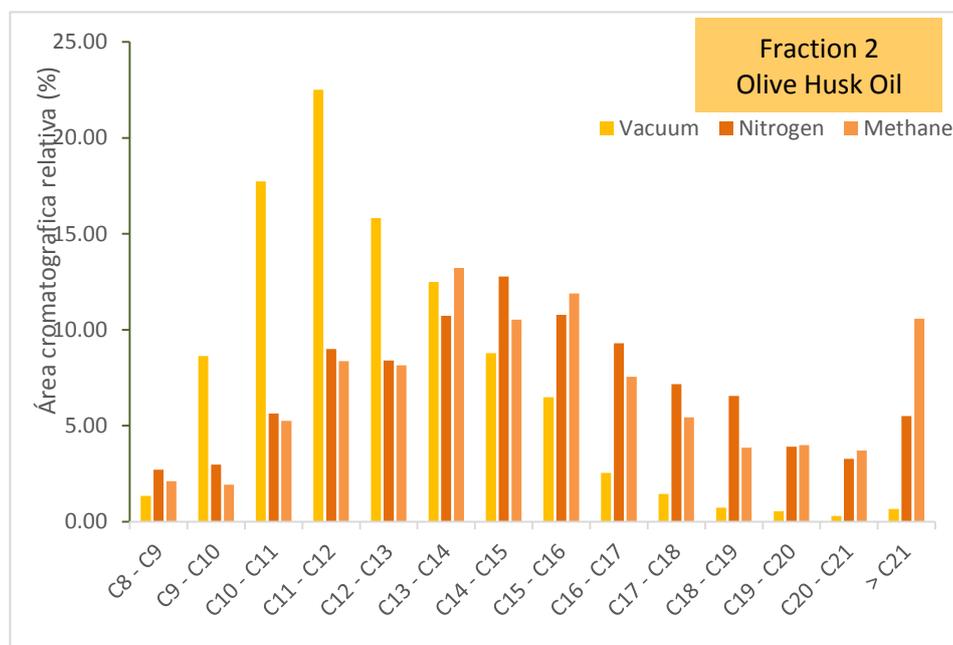
***Figure 26.*** *Carbon number distribution of the distilled bio-oil components (Fraction 2), from the pyrolysis of olive husk oil at 3 bar, during 10 min, under different atmospheres.*
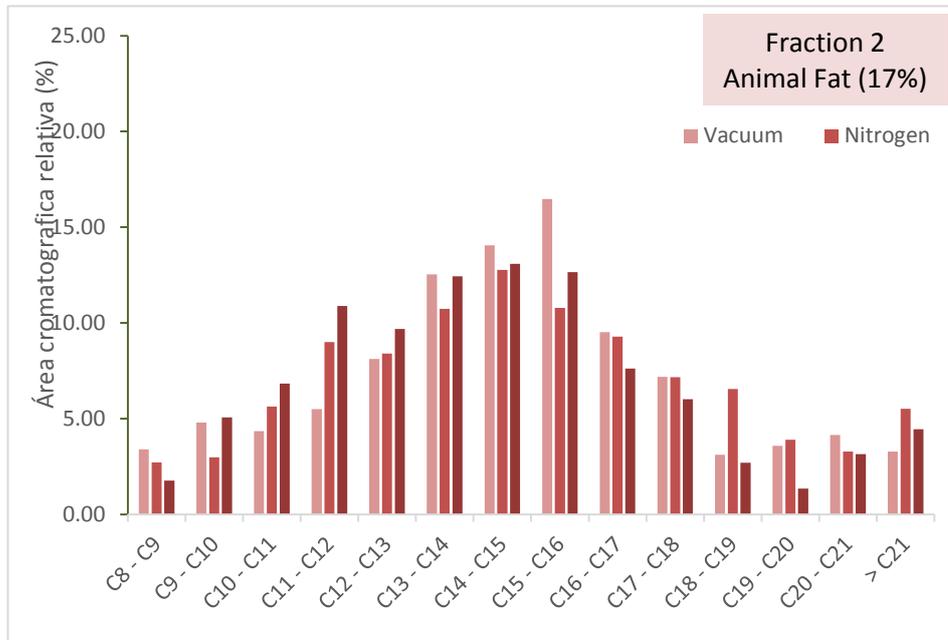
Figure 27. *Carbon number distribution of the distilled bio-oil components (Fraction 2), from the pyrolysis of animal fat (17%), at 3 bar, during 10 min, under different atmospheres.*

Totally different are the fatty acid profiles for the 2nd fraction of distillation. It is quite notable the fact that the fatty acid concentrations are quite low, reaching only up to 15% maximum for *olive oil* in all atmospheres. The biggest fatty acid concentration is noted from C13 to C16 for all atmospheres, reaching 15% for C15 – C16 in vacuum atmosphere. Afterwards there is a gradual drop in the concentration of fatty acids for all oils.

Regarding the 2nd fraction of *olive husk oil*, now, quite noteworthy is the fact that the highest fatty acid concentrations (up to 23%) are noted in a vacuum atmosphere for the fatty acids C10 – C13. Afterwards, in the vacuum atmosphere there is a gradual reduction in the fatty acid concentration. In both nitrogen and methane atmospheres, though, the highest amount of fatty acids is noted between C11 – C17, reaching up to 12 % for both.

Regarding the fatty acid profile of *animal fats (17%)* it is important to note that the highest fatty acid concentrations are noted in the area from C11 to C17, reaching

the top peaks of C15 – C16 for the vacuum atmosphere (~16%) and of C14 – C15 for both nitrogen and methane, up to 13% for both.

Also, for fraction 2 of the olive oil derived bio-oil the influence of methane resulted in a higher content of lower molecular weight components up to C16 and reduction of the components with higher number of carbons.

Like previously observed for Fraction 1 the stabilization of lower molecular weight products is not observed for olive husk oil as in the case of olive oil or animal fat.

The animal fat is also influenced by the methane atmosphere during pyrolysis presenting a higher stabilization of the lower molecular weight components of the bio-oil, up to 15 carbon atoms. This stabilization may result from direct reaction of methane with the primary pyrolysis products or from the *in situ* formation of hydrogen by pyrolysis of methane that in turn will react with the primary products of pyrolysis, stabilizing them and reducing the extent of the recombination reactions.

Once more, the same figures as previously are presented, viewed under different atmospheres.
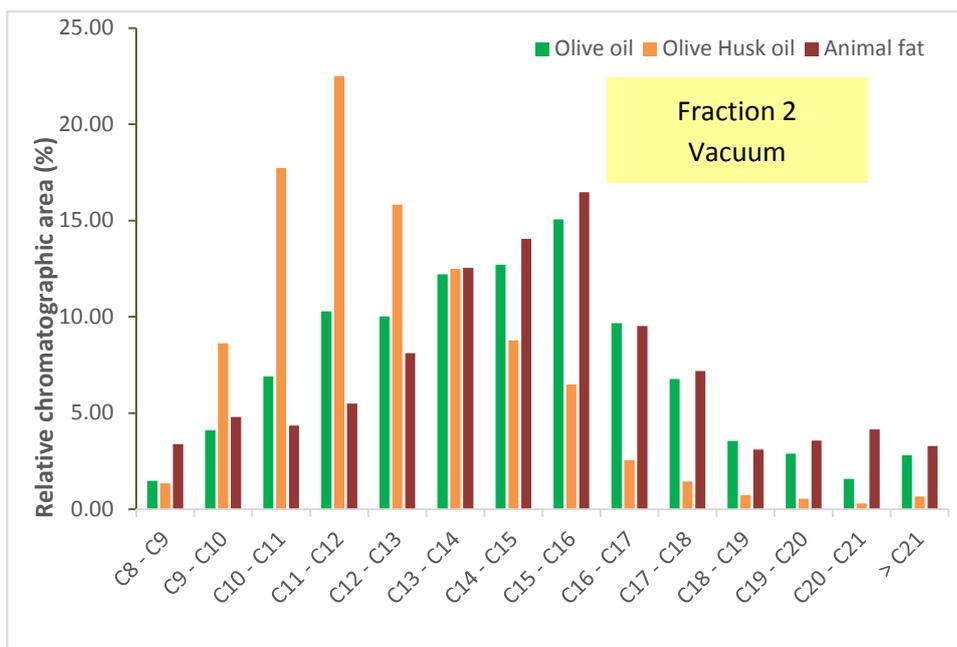
Figure 28. *Carbon number distribution of the distilled bio-oil components (Fraction 2), from the pyrolysis of all oils, at 0 bars, during 30 min, under vacuum atmosphere.*
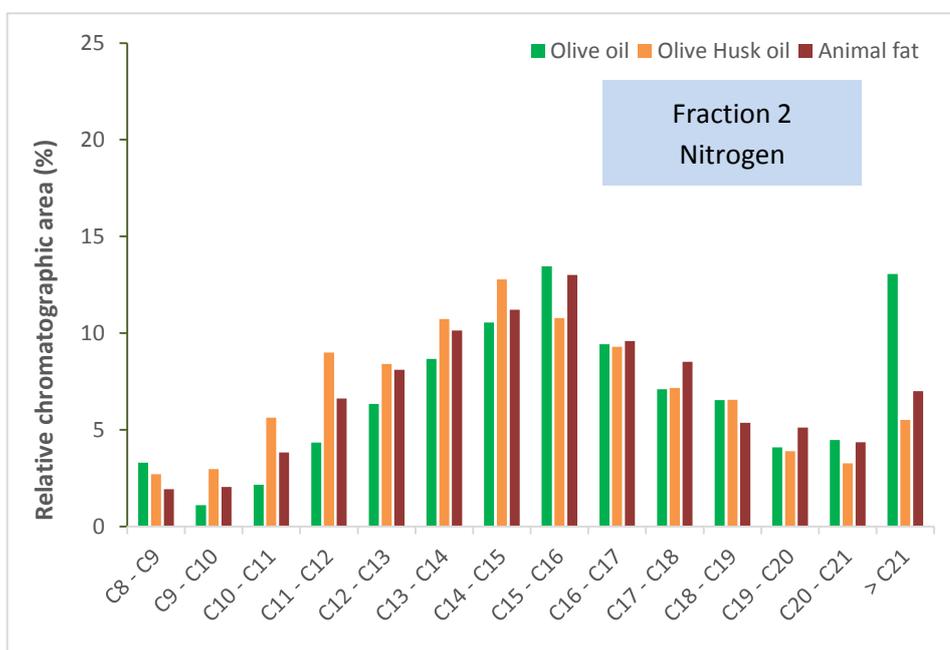

Figure 29. *Carbon number distribution of the distilled bio-oil components (Fraction 2), from the pyrolysis of all oils, at 3 bars, during 10 min, under nitrogen atmosphere.*
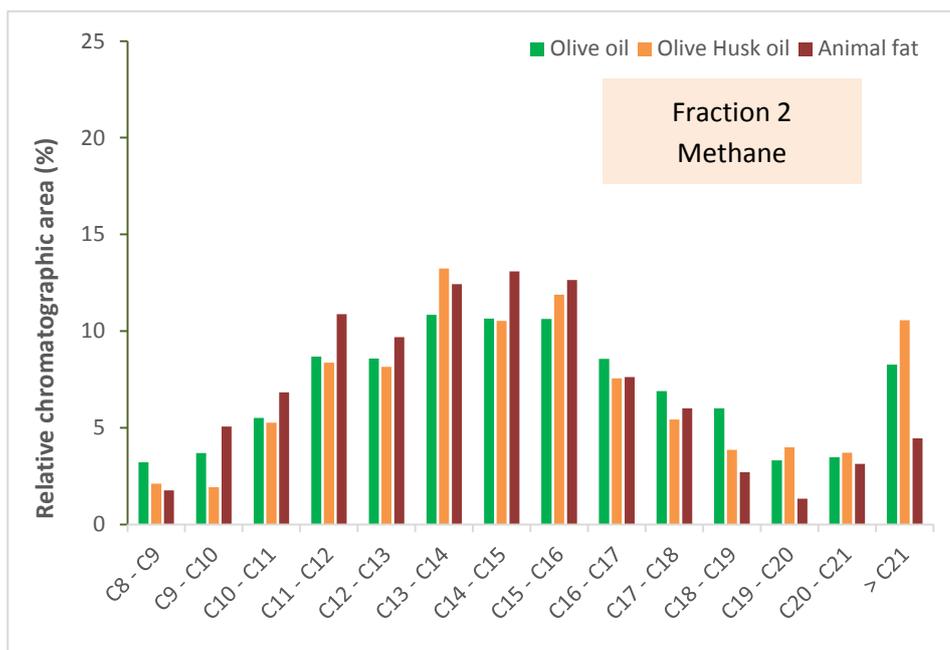
Figure 30. *Carbon number distribution of the distilled bio-oil components (Fraction 2), from the pyrolysis of all oils, at 3 bars, during 10 min, under methane atmosphere.*

## 5.2 Total distillation yields for every oil under all atmospheres
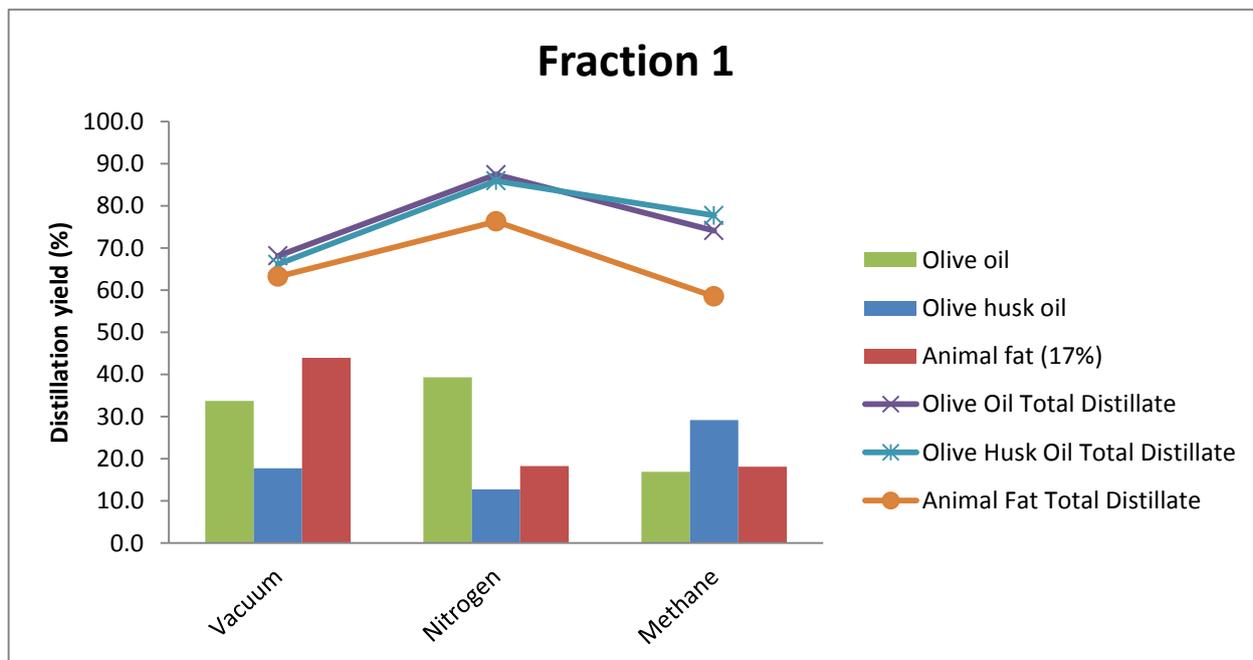
Figure 31. *Distillation yields of the distilled bio-oil components (Fraction 1) in comparison to total distillate, from the pyrolysis of all oils, under all atmospheres*

Taking into account *Figure 31* it is quite obvious to understand that for the 1st fraction of distillation, *vacuum* atmosphere is the one that gives relevantly high distillation yields, reaching even the percentage of 44% for animal fats and 34% for olive oil. Generally, olive oil is the one that seems to have the highest yields compared to the other oils and fats, whereas olive husk oil is the one that seems to give higher yields in a methane atmosphere.
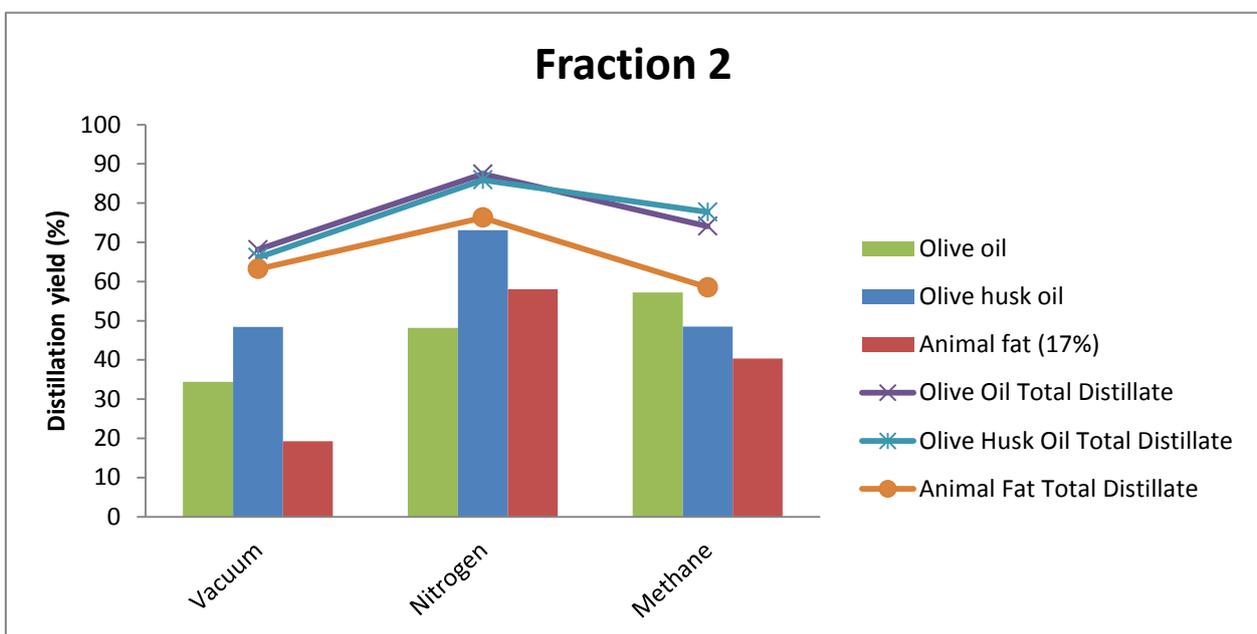
Figure 32. *Distillation yields of the distilled bio-oil components (Fraction 2) in comparison to total distillate, from the pyrolysis of all oils, under all atmospheres*

Remarkably different is *Figure 32,* where the distillation yields of fraction 2 are presented. The highest yields are those of *olive husk oil* and *animal fats (17%)* under a nitrogen atmosphere, reaching respectively 76% and 58% in relevance to the total distillate in these conditions which is 86% for olive husk oil and 77% for animal fats. Moreover, quite remarkable is the fact that olive oil presents the highest distillation yield under a methane atmosphere, reaching 58% while the total distillate in this

atmosphere is 75%. Last but not least, the vacuum atmosphere presents quite low yields for fraction 2, not being able to surpass beyond 49% of olive husk oil.

6. CONCLUSIONS

6.1 General conclusions

As previously mentioned, the aim of this study was not to define if the distillates produced through the experimental procedures are biodiesels, but to examine if two basic properties of theirs are similar to those of pure diesel; namely the contained –in the bio-oils– methyl esters and the estimation of the distillation yields of those bio-oils.

Moreover, among the aims of this research has been to estimate which of the three vegetable oils and animal fats could more effectively meet those diesel properties as well as to determine under which atmosphere these properties could be better met.

6.1.1 Conclusions for the oils and fats

Generally, due to the different conditions and atmospheres in which the experiments were carried out, it is quite difficult to determine which is the oil or fat that best meets the diesel properties.

So, regarding the first fraction of the distillation, all oils and fats have quite similar concentrations in fatty acids with minor variations. What can be noted though, is that *olive husk oil* presents the highest concentrations in both vacuum and nitrogen atmospheres. Regarding the second fraction, now, olive husk oil is again making the difference, in the – generally similar between them – fatty acid profiles because it is noted that, under a vacuum atmosphere, reaches a fatty acid concentration of 23% for carbon numbers from 11 to 12. All in all, as a total distillate yield, we can observe that for fraction 2, the biofuels produced are reaching quite high distillation yields, reaching even 85%.

As a result, *olive husk oil* is the one that achieves the highest distillation yield of both fractions almost under all atmospheres and especially under the nitrogen one.

6.1.2 Conclusions for the experimental atmospheres

Taking a look at *Figure 32* it is quite obvious to see that the nitrogen atmosphere is the most efficient, reaching quite high distillation yields up to 85%; quite high for a biofuel. Moreover, is obvious that for the first fraction, the most suitable atmospheres are methane and vacuum for olive oil, even though the concentrations that it reaches are up to 30% and methane for animal fat, again with concentrations up to 33%. The use of methane resulted in a stabilization of the lower molecular weight components of fraction 1, namely with 8 to 10 carbon numbers, for the bio-oils obtained from animal fat (17%) or olive oil, whereas, in the second fraction of distillation, what can be concluded from the fatty acid profiles is that they generally do not reach high fatty acid concentrations.

At this point, it is quite noteworthy to add that the different pyrolysis times as well as pyrolysis pressures did not make a significant effects on the bio-oils produced. There were some repetitions performed at the laboratory, changing a few variables in the tests, such as performing the olive oil test under vacuum conditions for 20 mins instead of 30 mins, or using an aviary fat of 4.5% acidity instead of 17% acidity, or performing the animal fat experiments in 20 mins instead of 10 mins. In every case, the variations in pyrolysis yields, distillation yields and fatty acid profiles were minor. As a result, there is no point in alternating the experimental conditions.

6.2 Difficulties and Restrictive Factors of Research

Some of the difficulties and restrictive factors of this research are listed below:

- The fact that, in order to check all the diesel properties of a bio-oil much equipment, time and effort is needed and it is quite difficult to be performed in a university laboratory.
- The absence of the needed equipment so as for the diesel properties to be checked. The properties needed to be checked are listed on *Table 1.*
- The time limit of the experiments, since they were performed, as previously mentioned, in an Erasmus programme that lasted for a whole semester.

6.3 Suggestions for future research

At this point, it would be very crucial for further, future research suggestions to be given.

As previously mentioned, due to the lack of available equipment, as well as time, elementary analysis and chemical composition of the produced bio-oils could not be performed. So, samples of the produced bio-oils could be sent to relevant laboratories to determine their accurate composure and have it compared to the Biodiesel 14214 European Standards (*Table 5).* This would be a very useful addition for a future research.

Moreover, again due to lack of time and equipment, there was not biofuel quality checking performed. The biofuels produced from both vegetable oils and animal fats were not subjected to further analysis regarding their properties, such as: calorific value-high heating value, acidic value, pH measurement, water content. This would be a quite important addition ad should be taken into consideration to be performed to all biofuels produced in the future.

So, although the upgraded bio-oil could be used as alternative fuel of boiler in internal combustion engines, it still cannot replace the fossil fuels completely due to few restrictions in technologies and in cost. So, it is quite a big matter the way with which the upgrading technologies could be used and upgraded so as the bio-oil from biomass pyrolysis could be directly used, especially for the case of *aviary oil (animal fat 17%).*

Animal fats, generally, contain more protein and phosphoacylglycerols (gums) due to the fact that they are animal cell membranes and thus remain within the lipids fraction. For this reason, a degumming process could be used in order to eliminate the phosphoacylglycerols from fats, prior to biodiesel production. A very efficient process, so far, is using 60% orthophosphoric acid, after which there can be performed centrifugation so as to separate the gums

Furthermore, biodiesel produced from animal fats is quite less stable for oxidation, in addition to it lacking natural antioxidants compared to vegetable originated biodiesel. For these properties, biodiesel produced from animal fats might not be adequate to use it 100% pure in vehicles during cold weather. However, it is possible that it might be used 100% pure in boilers for heat generation. [Sendzikiene et al., 2005]

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