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Bio-Hydrocarbons through Catalytic Pyrolysis of Used Cooking Oils: towards sustainable jet and road fuels

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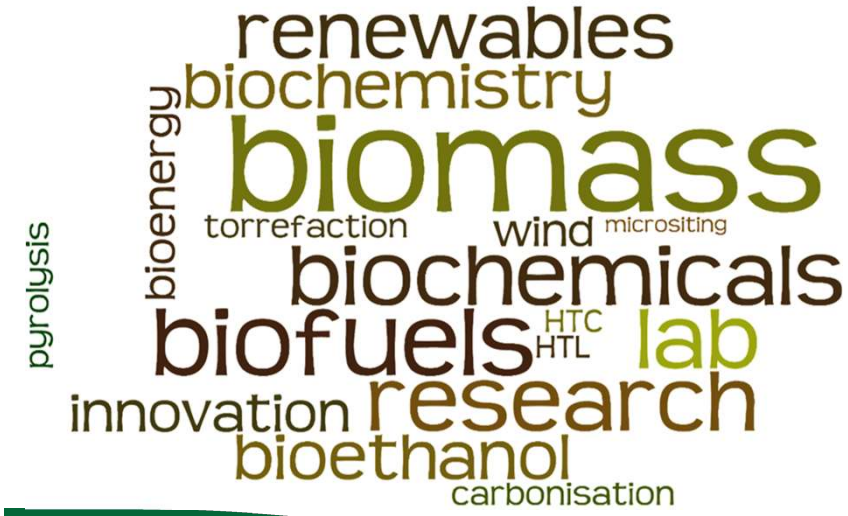

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Renewable Energy Consortium for Research and Development
Florence, Italy

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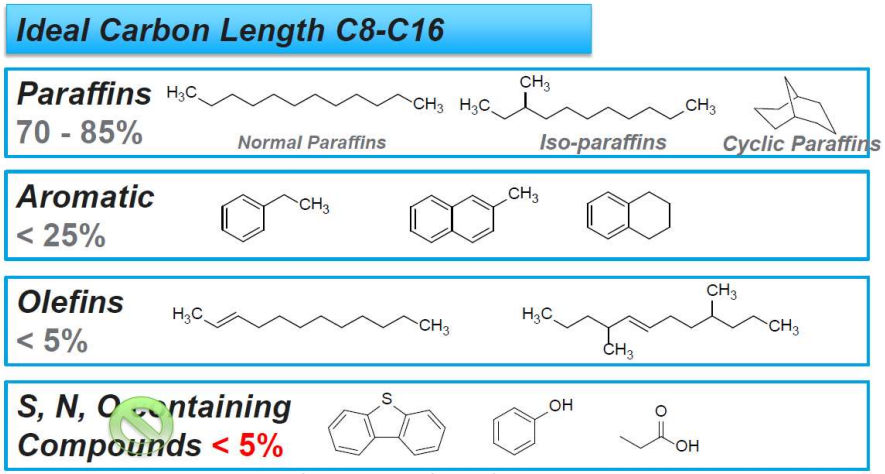
Outline of the presentation

- Introduction
- Experimental set-up
  - Pyrolysis unit
  - Process conditions
- Preliminary experimental results
  - Yield
  - Composition
  - Distillation test
- Conclusions & Outlook

Introduction

Jet fuel specification

Jet fuel: HCs profile



www1.eere.energy.gov/bioenergy/pdfs/holladay_caafi_workshop.pdf

Jet fuel: chemical and physical properties

Parameters	Limit
Flash point	> 38 °C
Crystallization (freeze) point	< - 47 °C
Viscosity at – 20 °C	< 8 mm^2/s
Low calorific value	> 42.8 MJ/kg

DEFSTAN 91/91

➢ **Bio-jet fuel** must meet the aviation specification as a **drop-in fuel!**

Scope of the work

RE-CORD focuses on investigation & testing of **used cooking oils** (such as fried cooking oil) as feedstock for alternative thermochemical process.

Used cooking oil

How?

Distilled fraction

Routes to green fuels

Some routes to produce biojet fuel from UCO and/or vegetable oils (e.g. **NExBTL** [NESTE OIL], **ECOFINING** [UOP-ENI]):

Technology	TRL	Products
Fischer Tropsch process	COMMERCIAL	FT SPK (Fischer–Tropsch Synthetic Paraffinic Kerosene)
Hydrotreated VOs (HEFA)	COMMERCIAL	Green jet fuel (drop-in)

→ **High OPEX!**

Routes to green fuels

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Commercial hydrotreating of VOs

RE-CORD alternative process

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Experimental set-up

Literature review

Poster: Buffi M, Rizzo AM, Chiaramonti D.
A review on renewable jet fuel from thermo-chemical conversion of vegetable and cooking oil. Pyro2014.

- Target: maximizing **yield** and **quality** of **bio-kerosene fraction**;
- **4 catalysts** and **2 WHSVs** have been selected by means of literature review.

Materials & Methods

- Feedstock
  - ✓VO, UCO, FA
- Test conditions
  - 2 process T (500 – 550 °C)
  - 4 different catalysts (CAT1-4)
  - 2 WHSV (2.5-4)
- Liquid characterization
  - GC/MS + GC/FID (*to be concluded…*)
  - Lab distillation

Feedstock: VO, UCO, FA mixture

Parameter	Unit	VO (Sunflower)	UCO (Filtered)	FA Mixture
Viscosity at 40 °C	mm^2/s	26.0	38.15	18.03
Acid value	*mg KOH/g*	1.06	2.63	201.7
Free Fatty Acid	*%*	0.53	1.31	100.85
Water content	*%*	0.085	0.08	0.08
Total contamination	*mg/kg*	209	256	68
Phosphorus	*mg/kg*	0.11	10.1	
C	*%*	77.8	76.3	76.3
H	*%*	11.9	11.7	12.2
N	*%*	0.01	0.02	0.02
N	*mg/kg*	116	137	
O	*%*	10.3	11.98	11.48
LHV	*MJ/kg*	37.0	36.4	36.8

FAs	%wt	
Capric	0.09	*C10:0*
Lauric	2.83	*C12:0*
Mystiric	1.43	*C14:0*
Palmitic	4.03	*C16:0*
Stearic	1.17	*C18:0*
Oleic	61.8	*C18:1*
Linoleic	13.5	*C18:2*
Linolenic	0.38	*C18:3*
Erucic	6.41	*C22:1*
unidentified	8.38	-

Experimental setup

- ✓ Pyrolysis unit + catalytic section
- ✓ Capacity up to 1.5 kg/h;
- ✓ Up to 600 °C (500 °C);
- ✓ Electrically heated;
- ✓ Modular condensation line;
- ✓ T, p, gas composition (CO, H2, CO2).
- ✓ WHSV = 2.5 – 4 h^{-1}

RE-CORD/CREAR pyrolysis unit in Florence (ITA)

Experimental procedure

Feedstock	Test N.	Catalyst	Temperature	WHSV
-	*n*	-	*°C*	*1/h*
UCO	1	none	500 - 500	-
UCO	2	Catalyst nr. 1		4
UCO	4	Catalyst nr. 2		4
UCO	5	Catalyst nr. 3		4
UCO	6	Catalyst nr. 4		4
UCO	7	Best performing		2.5
FA	8	Best performing		2.5

- ✓ UCO conversion. **Bio-oil** quality vs **catalyst**
- ✓ **Best configuration** tested again by **increasing** catalyst mass (WHSV).
- ✓ Best **bio-oil distilled** to identify **bio-kerosene fractions**.
- ✓ FA tested to compare deoxygenation behaviour vs UCO

Results

Bio-oil properties (extract)

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Feed rate = 1.5 kg/h

Temperature = 500°C

Duration = 90 min

WHSV = 4 h^{-1}

		Catalyst				
Parameter	**Unit**	**None**	**CAT n.1**	**CAT n.2**	**CAT n.3**	**CAT n.4**
Feedstock		UCO	UCO	UCO	UCO	UCO
WHSV	*1/h*		4	4	4	4
Process temperature	*°C*	500	500	500	500	500
Liquid yield	*wt%*	62.70	63.64	54.55	33.74	61.72
C	*wt%*	76.75	76.10	76.03	77.90	78.17
H	*wt%*	11.45	11.10	11.65	10.10	11.48
N	*wt%*	0.02	0.03	0.08	0.07	0.03
O	*wt%*	11.98	12.77	12.25	11.93	10.33
Water content	*wt%*	0.89	0.77	1.18	8.36	1.61
Density	*kg/liter*	0.87	0.85	0.85	0.90	0.86
LHV	*MJ/kg*	36.82	37.79	39.57	36.48	37.46
Acid value	*mg KOH/g*	117.73	74.10	61.97	20.45	80.07
Kinematic viscosity (40°C)	*cSt*	4.47	2.24	3.36	1.19	5.68

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Bio-oil composition

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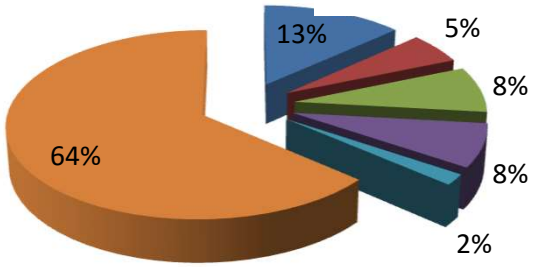
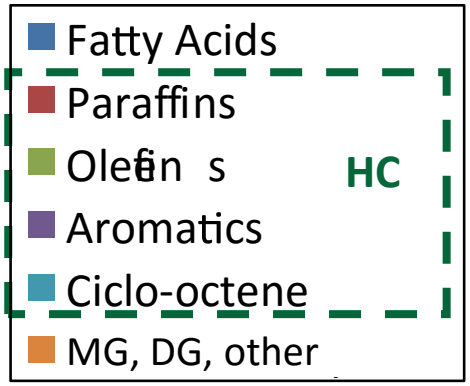
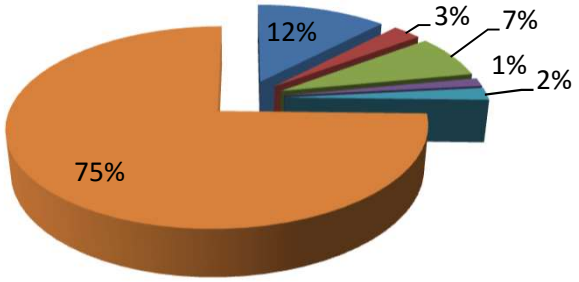
- ✓ The identification and quantification of chemical species were carried out by means of GC MS / GC FID (GC 2010 Plus – Shimadzu)

CAT n.1 **23 % HC**

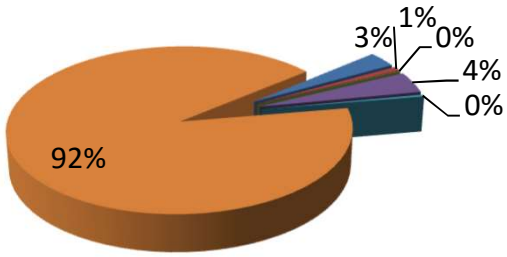




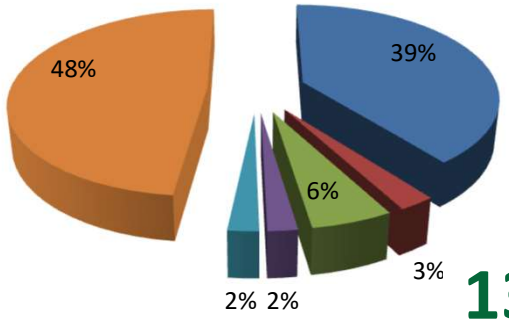
CAT n.2



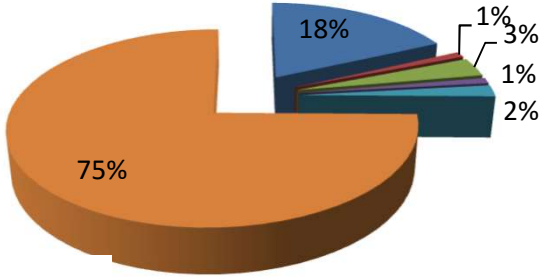
CAT n.3



NO CAT



CAT n.4



13 % HC

Test with **CAT n.1** @500°C selected as best case in terms of **liquid yield** and **composition**

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Increasing catalyst mass…

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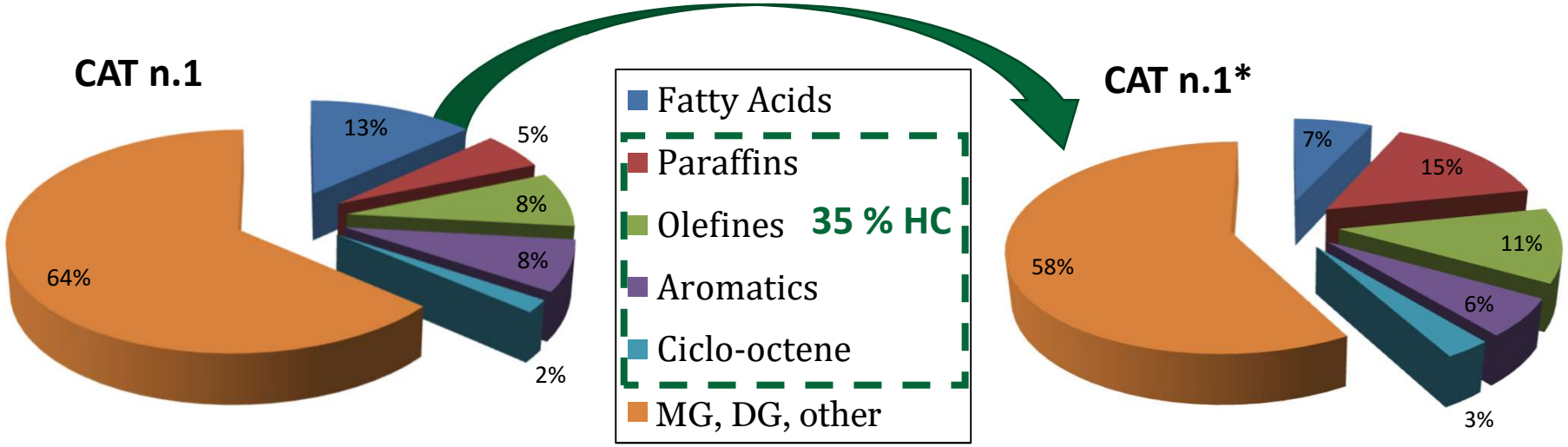
✓ Best configuration (**CAT n.1**) tested at 500 °C, **WHSV = 2.5 h^{-1}**(**CAT n.1***)



Increasing catalysts mass:

✓No significant changes in yield (~ 63 %)
✓**higher in aliphatic** HCs
✓ lower in aromatic HCs
✓ **lower** in FFAs

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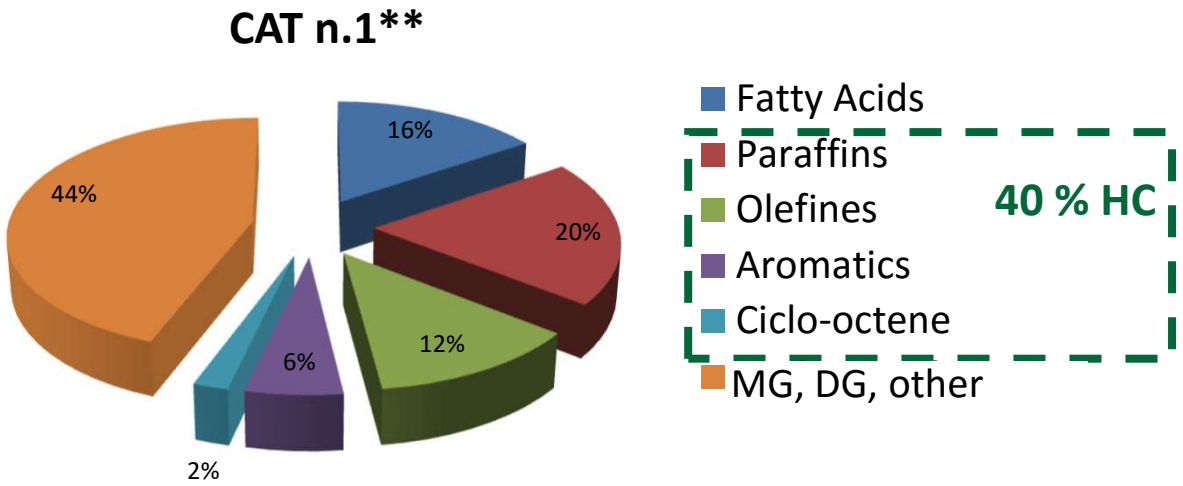
FAs test

Test **CAT n.1*** (UCO) was repeated feeding **FAs** @ 500 °C and WHSV = 2.5 h^{-1} (**CAT n.1****)



- **Reduced liquid yield** (~ 49 vs 63%).
- **Higher HCs content**
- **Higher Paraffins & Olefins content**

Cromatogram (CAT 1*)

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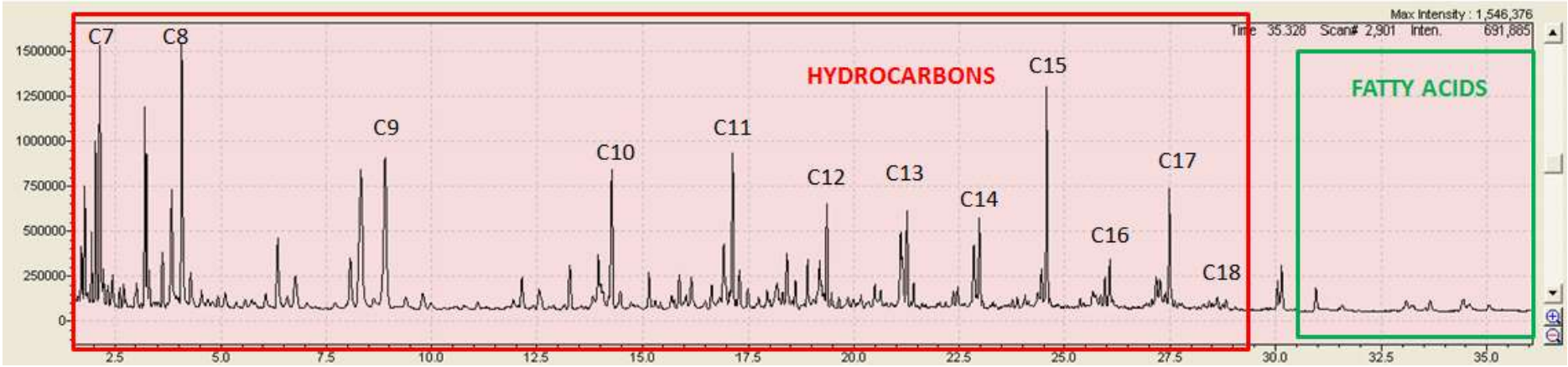
@500°C, UCO, CAT 1, WHSV=2.5 h^{-1}



- Higher peaks consist in **paraffinic** HCs
- **C7**, **C8** and **C15** make up the **larger** fraction of HCs in bio-oil

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UCO vs FA pyrolysis

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Oxygen removal is significantly higher

Parameter	Unit	Filtered UCO (1 µm)	FAs
Density	*kg/m³*	911	
Kinematic Viscosity at 40 °C	*mm²/s*	38.15	18.03
Acid value	*mg KOH/g*	2.63	201.7
Free Fatty Acid	*%*	1.31	100.85
Water content	*%*	0.08	0.08
Ash	*% (m/m)*	0.01	
Total contamination	*mg/kg*	256	68
Insoluble impurities	*%*	0.05	
Phosphorus	*mg/kg*	10.1	
C	*%*	76.3	76.3
H	*%*	11.7	12.2
N	*%*	0.02	0.02
N	*mg/kg*	137	
O	*%*	11.98	11.48
Calorific value, lower	*MJ/kg*	36.4	36.8

Parameter	Unit	Norm	CAT 1*	CAT 1**
Feedstock			*UCO*	*FAs*
WHSV	*1/h*		*2,5*	*2,5*
Catalyst Temp.	*°C*	-	*500*	*500*
Liquid yield	*wt%*	-	*63,41*	*48,82*
C	*wt%*	*UNI 15104*	*76,295*	*83,53*
H	*wt%*	*UNI 15104*	*11,5*	*12,7*
N	*wt%*	*UNI 15104*	*0,04*	*0,04*
O	*wt%*	*calculated*	*12,165*	*3,73*
Water content	*wt%*	*UNI 8534*	*0,5345*	*0,17*
Density	*kg/liter*	*UNI 3675*	*0,843*	
LHV	*MJ/kg*	*calculated*	*38,897*	*40,0976*
HHV	*MJ/kg*	*DIN 51900-2*	*41,335*	*42,79*
Acid value	-	*UNI 14104*	*51,445*	*44,4*
Kinematic viscosity (40°C)	*cSt*	*UNI 3104*	*2,48*	*1,5*
Fatty Acids	*wt%*	*wt%*	*7%*	*16%*
Paraffins	*wt%*	*wt%*	*15%*	*20%*
Olefines	*wt%*	*wt%*	*11%*	*12%*
Aromatics	*wt%*	*wt%*	*6%*	*6%*
Ciclo-octene	*wt%*	*wt%*	*3%*	*2%*
Tot. HCs	*wt%*	*wt%*	*35%*	*40%*
SUM	*wt%*	*wt%*	*42%*	*56%*

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Distillation test: procedure

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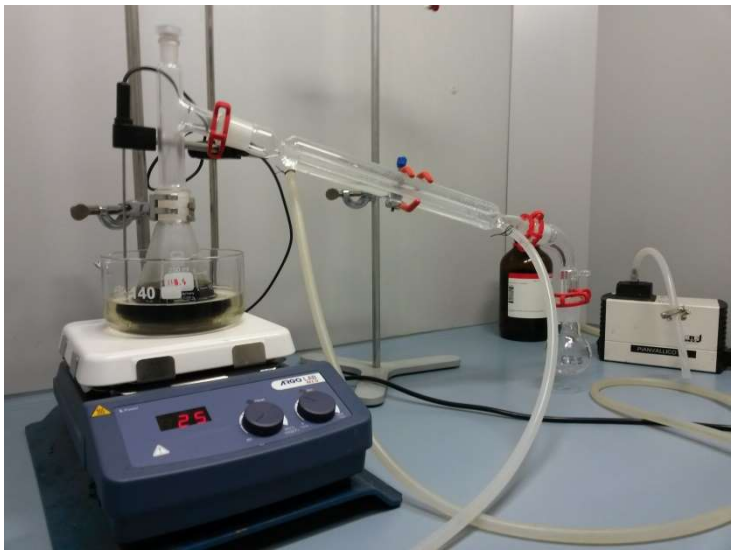
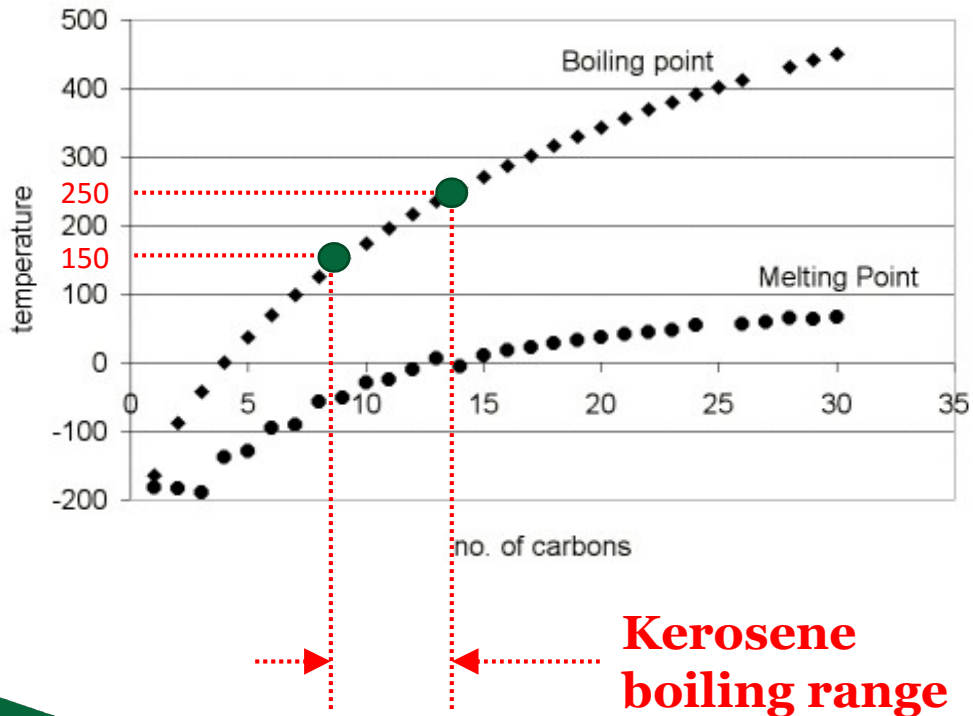
- ✓ Distillation test (p_atm, CAT n.1*, 500 °C, WHSV = 2.5 h^{-1})
- ✓ 4 fractions: **A** (<150°C); **B** (150-200°C); **C** (200-250°C) + residue



Distillation set-up

- ✓ Distillation curve of paraffinic HCs



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Distillation test: UCO - CAT1*

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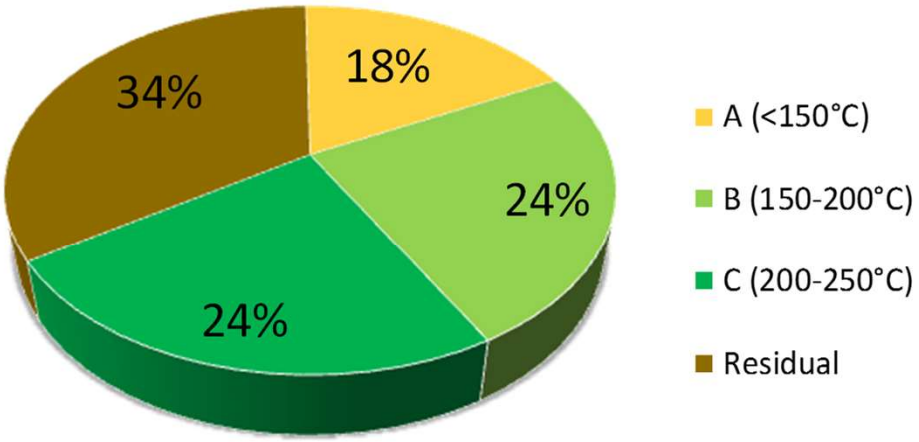
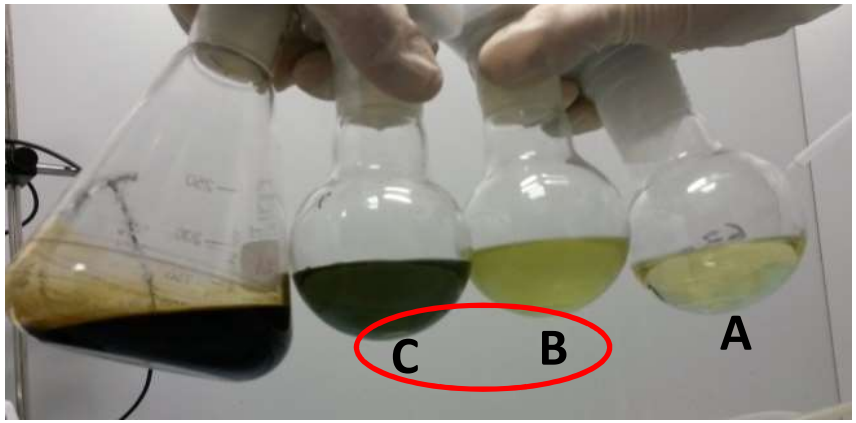
Yields of separated fractions





- Bio-intermediate in the range of kerosene fraction **48%** (B + C), i.e. 30% of total feed

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Conclusions

Conclusions

- **Catalytic conversion** through pyrolysis of UCO was performed at 500°C with 4 different catalysts (WHSV = 4 h^{-1}).
- The best result (CAT n.1) gave **63.6 %wt of bio-oil**, with **lower O_2**, **density**, **viscosity** and **higher HV** than original feedstock.
- By increasing catalyst mass, **no significant changes** in terms of **bio-oil yield were observed**, but **larger** amount of **HCs** classes were detected (from 24 to 35%wt of recovered bio-oil).
- **Distillation fractions in the range of kerosine** showed promising properties (HC, composition)

Further steps…

- **Improve** analytical tecniques for bio-oil analysis.
- **Increase** yield (reactor / feeding system redesign).

Acknowledgements

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Partners of ITAKA project

SILO SpA for UCO

Thanks for your Attention!

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- **Public-private no-profit research center**
  - ✓ **K182 Chemical Lab, fully dedicated to Biomass, Bioproducts and Renewables**
  - ✓ **Pilot Plants**
- **<u>Members</u>:**
  - ✓ **Univ. of Florence** *(**CREAR** & **Montepaldi**)*,
  - ✓ **Spike Renewables**
  - ✓ **Pianvallico** *(Mugello Municipalities, Florentine Metropolitan area)*

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CREAR & RE-CORD: some figures…

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Budget (contributions) from R&D activities on Biomass/Renewables:	
CREAR (2002-2015)	> 6.1 M€
RE-CORD (2012-2015)	≈ 2 M€
EU/Internat.Projects	14 *(3 Coord)*
National Projects	9 *(4 Coord)*

Patents related to the research work of RE-CORD/CREAR personnel	
Nr of patents	6

Publications	
Journal papers	>30
Conf.Proceedings (ISI Indexed)	12
Conf.Proceedings	108
Edited Intern.Conf.Proceedings	3
Magazines	7
Thesis	>64
Studies (EC and Companies)	6

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Staff

President of RE-CORD

David Chiaramonti

Director of CREAR

Francesco Martelli

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EU FP7 ITAKA project

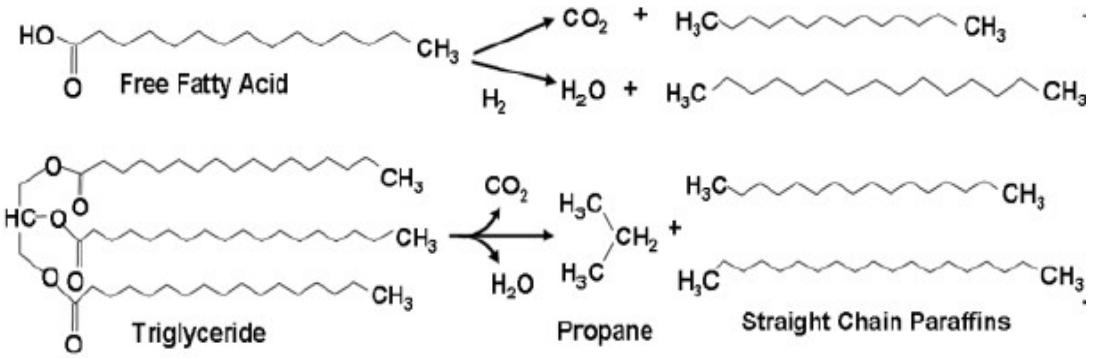
ITAKA is a collaborative project, aimed to produce **sustainable renewable aviation fuel** and to test its use in existing logistic systems and in normal flight operations in Europe.

Consortium members include companies and research centers leaders in: feedstock production (**BIOTEHGEN** and **Camelina Company España**); renewable fuel production (**Neste Oil** and **RE-CORD**); fuel logistics (**CLH** and **SkyNRG**); air transport (**Airbus**, **EADS IW UK**, **Embraer** and **SENASA**); and sustainability assessment (**EADS IW France**, **EPFL** and **MMU**).

Catalytic conversion route

The main goal consists on the investigation of the best catalytic conversion route through pyrolysis to maximize the production of **bio-intermediate** towards **bio-kerosene** (even as pretreatment for biorefinery).

- Kinetic mechanisms of cracking and species formation are strongly dependent by the catalysts adopted in pyrolysis.
- **<u>Target</u>: decarboxilation/ decarbonilation** of the triglycerides and FFAs molecules.



Triglycerides and FFAs decomposition.
Source: AltAir Fuels / UOP.

Distillation test: UCO bio-oil – CAT1*

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	Unit	Distillate A	Distillate B	Distillate C	Residual	Cross-check	Measured
Yield	*wt%*	0.18	0.24	0.24	0.34	1.00	1.00
C	*wt%*	81.50	69.70	70.60	78.20	74.93	76.30
H	*wt%*	12.20	10.20	12.00	11.50	11.43	11.50
O	*wt%*	6.28	20.07	17.36	10.27	13.61	12.17
N	*wt%*	0.02	0.03	0.04	0.03	0.03	0.04
Fatty Acids	*wt%*	**0.00**	**0.03**	**3.91**	**19.43**	7.55	6.86
Paraffins	*wt%*	26.69	20.12	21.77	6.28	16.99	14.88
Olefines	*wt%*	18.77	16.17	13.87	3.58	11.80	11.46
Aromatics	*wt%*	18.73	6.09	5.75	0.21	6.29	5.80
Ciclo-octene	*wt%*	3.31	2.47	1.26	0.00	1.49	2.88
Tot. HCs	*wt%*	**67.50**	**44.84**	**42.66**	**10.07**	36.57	35.03
%Recognized	*wt%*	**67.50**	**44.87**	**46.57**	**29.50**	44.13	41.88

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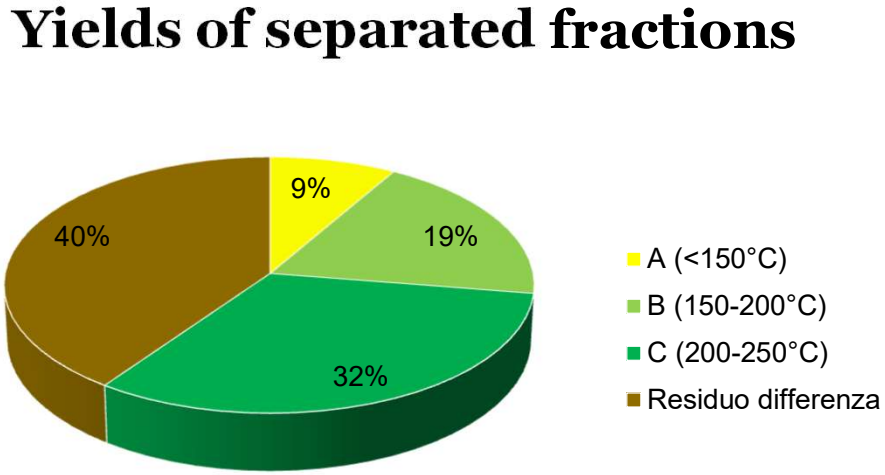
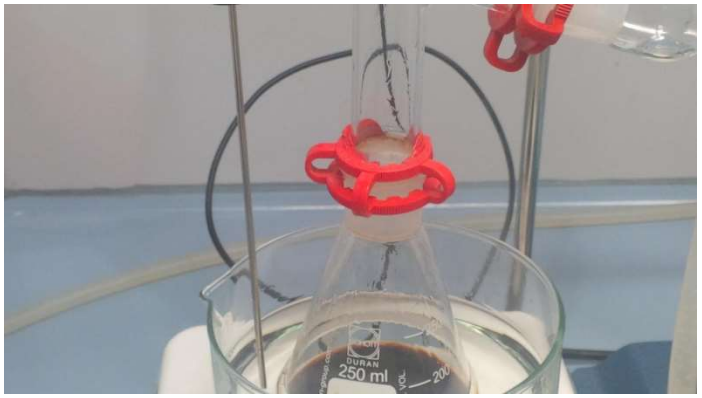
Distillation test: FAs – CAT1**





- Bio-intermediate in the range of kerosene fraction **51%** (B + C)

Distillation test: FAs – CAT1**

	Unit	Distillate A	Distillate B	Distillate C	Residual	Cross-check	Measured
Yield	*wt%*	0.09	0.19	0.32	0.40	1.00	0.00
C	*wt%*	83.43	85.59	86.82	80.68	83.83	83.53
H	*wt%*	12.27	12.56	12.89	10.34	11.75	12.70
O	*wt%*	4.21	1.83	0.27	8.96	4.40	3.73
N	*wt%*	0.09	0.0196	0.0194	0.0196	0.03	0.04
Fatty Acids	*wt%*	0.04	0.13	2.57	27.54	11.87	15.54
Paraffins	*wt%*	28.30	35.19	21.00	5.47	18.14	20.00
Olefines	*wt%*	28.34	16.71	14.50	4.48	12.16	12.46
Aromatics	*wt%*	16.55	12.14	5.53	0.39	5.72	5.66
Ciclo-octene	*wt%*	1.48	1.06	2.20	0.00	1.04	2.05
Tot. HCs	*wt%*	74.68	65.10	43.24	10.34	37.06	40.18
%Recognized	*wt%*	74.72	65.23	45.81	37.88	48.93	55.72