Blending of Hydrothermal Liquefaction Biocrude with Residual Marine Fuel: an Experimental Assessment

Arturo Di Fraia[1], **Andrea Maria Rizzo [1,2]** and David Chiaramonti [1,3]

[1] Renewable Energy Consortium for Research and Demonstration – RE-CORD, Viale Kennedy 184, 50038 Scarperia, Florence, Italy.

[2] DIEF, University of Florence, Department of Industrial Engineering, Viale Morgagni 40/44, Florence 50139, Italy

[3] Department of Energy "Galileo Ferraris", Polytechnic of Turin, I-10129 Torino, Italy

TCBiomass 2022 | Denver, Colorado | **April 19–21, 2022**

Summary

1. Background info and aim of the work

- Global and EU marine fuel market
- Current regulation and prospects
- EU sewage sludge management

2. Materials and methods

- Sewage sludge characterization
- RE-CORD HTL experiments with sewage sludge
- HTL products separation
- Blending tests

3. Results

- Analytical characterization
- Blend compliance with ISO 8217:2017

4. Conclusion and future works

Background information - Global and EU marine fuel market

Global maritime transport*
- 80% of global trade
- 6.1% of global oil demand
- 11 000 million of tons loaded

400 million ton/year of marine fuels

50 000 merchant ships

EU maritime transport [a,b]
- 35% of internal trades
- 75% of external trades
- 400 million passengers

43.6 million ton/y of marine fuels

*Concawe, “Marine fuel facts”, Environmental Science for the European Refining Industry, 2017
[a] Proposal for a REGULATION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL on the use of renewable and low-carbon fuels in maritime transport and amending Directive 2009/16/EC
[b] EUROSTAT Passengers embarked and disembarked in all ports by direction - annual data (2021)

Background information - Current regulation and prospects

GHG Emission
- 2 – 3% of global CO_2 emission [a]

EU Climate Target Plan (CTP)
- GHG reduction of 55% by 2030
- Carbon neutral by 2050

Renewable and low carbon fuel in maritime transport mix

2030	2050
6 – 9%	88%

FuelEU Maritime [b]
Proposal for a Regulation of the European parliament and of the council on the use of renewable and low-carbon fuels in maritime transport

- Obligation to use on-shore power supply or zero emission technology in ports under jurisdiction of a Member State
- Limit on yearly average greenhouse gas intensity of the energy used on-board by a ship during reporting period

* Concawe, "Marine fuel facts", Environmental Science for the European Refining Industry, 2017
** except for ship with sulphur abatement methods
[a] IEA Bioenergy, "Biofuels for the marine shipping sector: An overview and analysis of sector infrastructure, fuel technologies and regulations", 2017
[b] Directive 2009/16/EC

Background information - Global and EU marine fuel market

ISO 8217:2017

Distillate marine fuel
- Marine gas oil (MGO)
- Smaller and medium high speed units
- Lighter fraction of crude
- Seven grades (DMX, DMA, DFA, DMZ, DFZ, DMB, DFB)

20 – 30%
of total marine fuel demand[a]

Average price (2019)
647 $/ton*

Residual marine fuel
- Heavy fuel oil (HFO)
- Residue of the distillation process
- Six grades (RMA, RMB, RMD, RME, RMG, RMK)

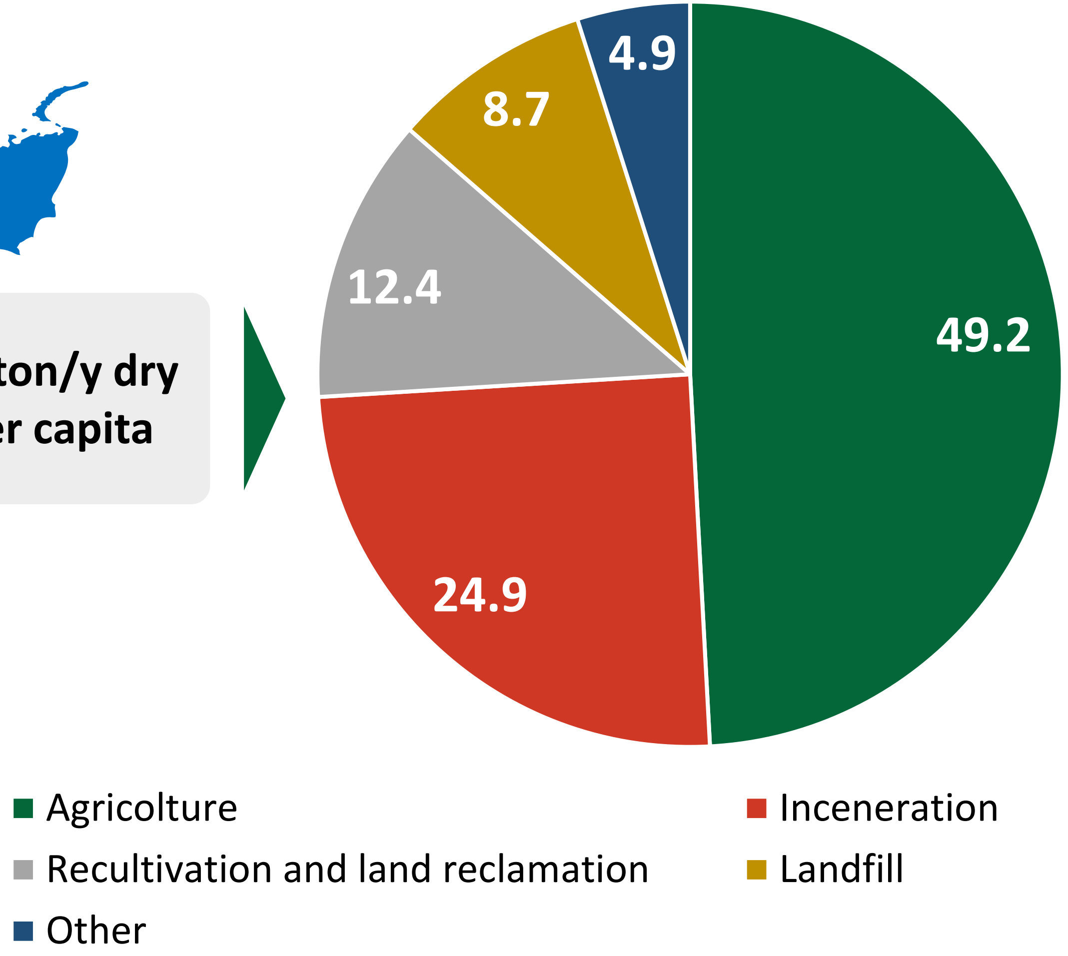
70 – 80%
of total marine fuel demand[a]

Average price (2019)
420 $/ton*

* average price of 2019 global Top 20 port "IMO 2020 What Every Shipper Needs To Know" (2019)
[a] Concawe, "Marine fuel facts", Environmental Science for the European Refining Industry, 2017

Background information - EU sewage sludge management

9 – 9.5 million ton/y dry
22.5 kg dry per capita



- Material recovery from SS in its infancy
- Increasing constraints on agricultural use

*data from Wareg - European Water Regulators, “Sludge management in the EU, following a circular economy approach”, 2019

Background information and aim of the work

Sewage sludge from wastewater treatment plant

Hydrothermal Liquefaction

Biocrude

Residual marine fuel ISO-F-RMG 380

Blending

Biofuel candidate

Preliminary Quality Assess

(FT-IR, composition)

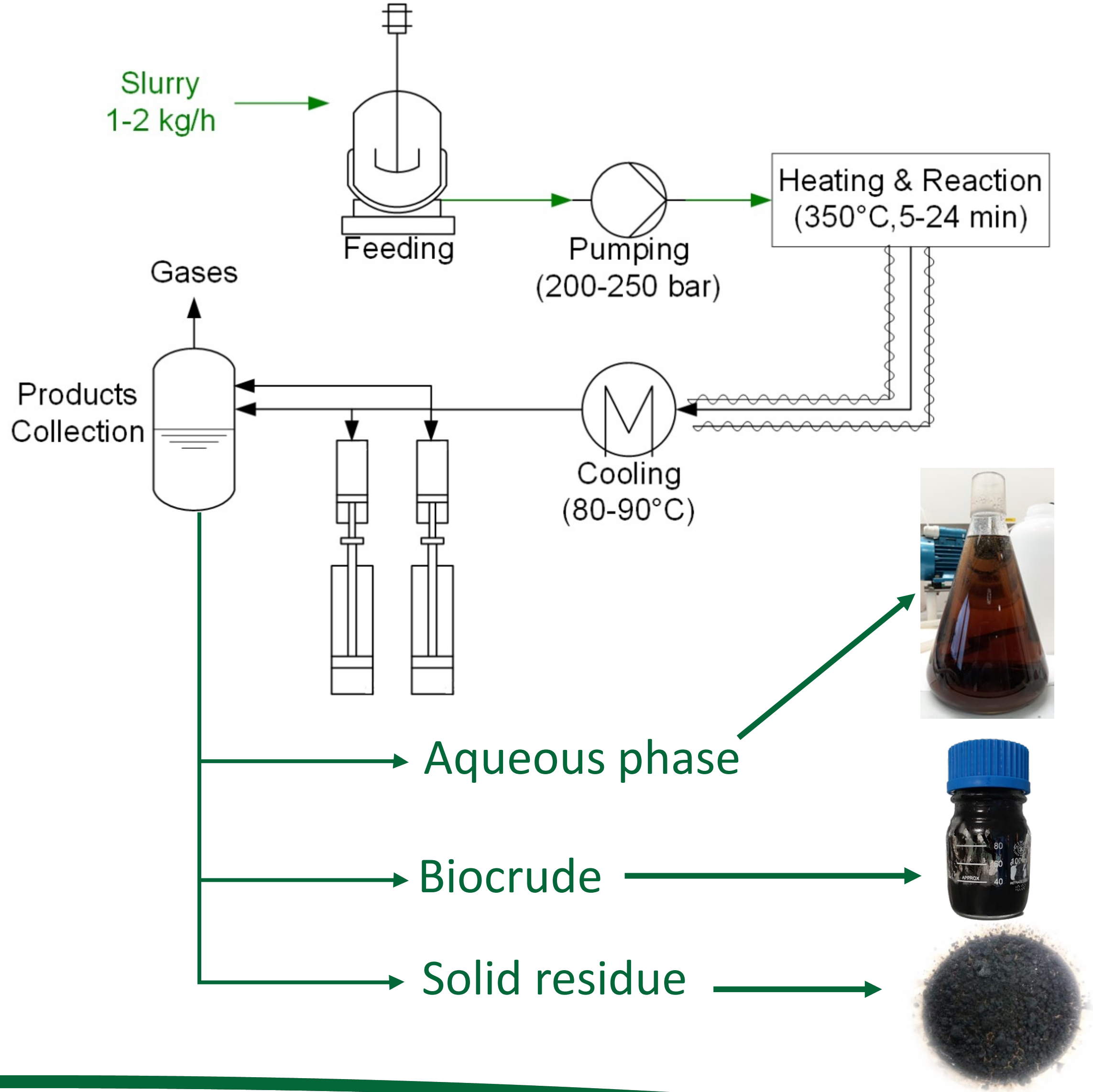
Materials and methods - Sewage sludge characterization

	Value
Moisture (wt.% w.b.)	71.1
Ash (wt.% d.b.)	19.8
Volatile matter (wt.% d.b.)	71.2
Fixed carbon (wt.% d.b.)	9.0
C (wt.% d.b.)	45.9
H (wt.% d.b.)	6.5
N (wt.% d.b.)	4.3
S (wt.% d.b.)	0.6
O (wt.% d.b.)	22.9

	Value
Si (mg/kg) d.b.	11996
Ca (mg/kg) d.b.	11066
Al (mg/kg) d.b.	7794
Fe (mg/kg) d.b.	5583
P (mg/kg) d.b.	5398
K (mg/kg) d.b.	2754
Mg (mg/kg) d.b.	2333
Ti (mg/kg) d.b.	769
Zn (mg/kg) d.b.	545
Na (mg/kg) d.b.	219
Ba (mg/kg) d.b.	194
Cu (mg/kg) d.b.	154

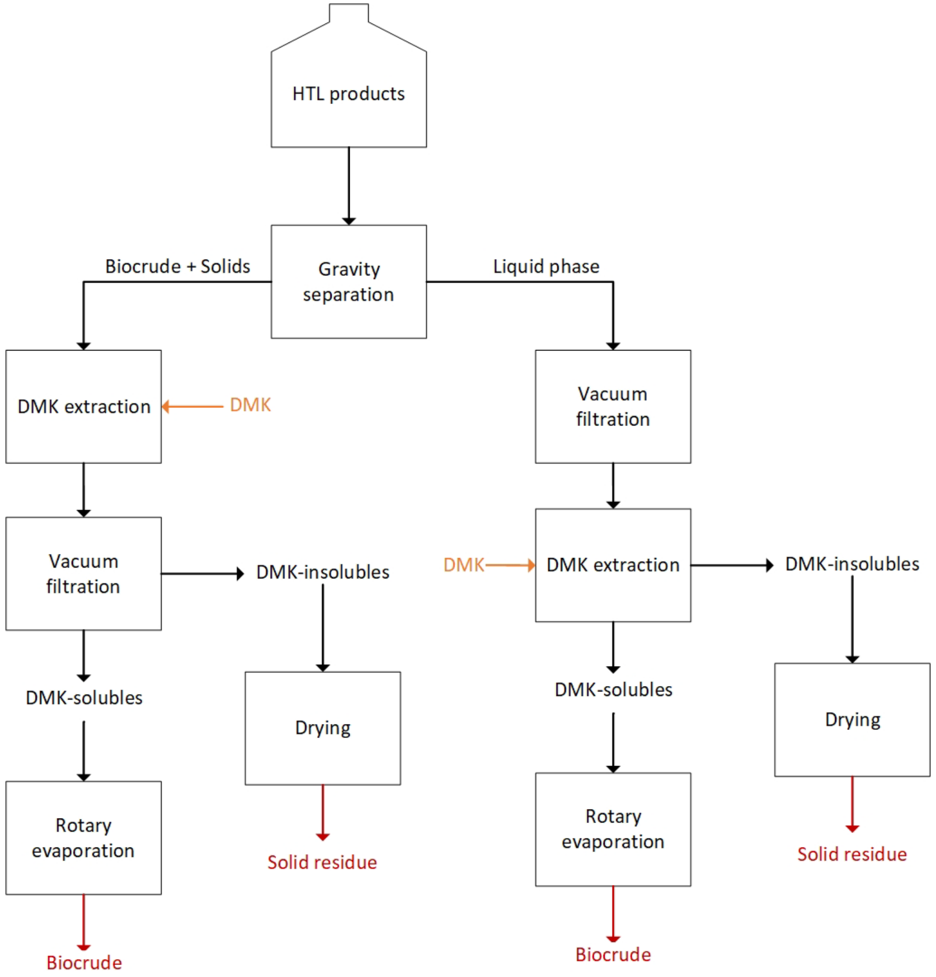
* Channiwala, S. A., Parikh, P. P. «A unified correlation for estimating HHV of solid, liquid and gaseous fuels»

Materials and methods - RE-CORD HTL experiments with sewage sludge



	Value	U.M.
Temperature	350	° C
Pressure	20	MPa
Residence time (RT)	5 – 20	min
Biomass-to-water ratio (B/W)	10	wt.%

Materials and methods - HTL products separation



	Value	U.M.
Temperature	350	° C
Pressure	20	MPa
Residence time (RT)	5 – 20	min
Biomass-to-water ratio (B/W)	10	wt.%

Materials and methods - Blending tests

	Marine fuel ISO-F-RMG-380	Biocrude	U.M.
C	87.1 (0.36)	75.7 (0.38)	wt.%
H	12.1 (0.16)	9.1 (0.04)	wt.%
N	0.2 (0.02)	4.6 (0.03)	wt.%
O	<0.5	10.1 (0.56)	wt.%
S	0.38 [a]	0.98 (0.01)	wt.%
Vanadium	6 [a]	1 (0.05)	mg/kg
Sodium	1 [a]	36 (0.25)	mg/kg

Absolute standard deviations in brackets.
[a] provided by the supplier;
n.a. = not analysed

	Blending test A	Blending test B	U.M.
Biocrude nominal content	10	20	wt.%

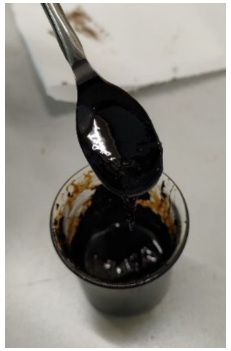
Marine fuel ISO-RMG-380

Biocrude

Heating 70 °C

Mixing

Blend



Results – Analytical characterization

Sample	C wt.%	H wt.%	N wt.%	O wt.%	S wt.%
SS biocrude	75.7 (0.4)[A]	9.1 (0.04)[B]	4.6 (0.03)[A]	10.1 (0.6)	0.98 (0.01)
Marine fuel	87.1 (0.4)[a]	12.1 (0.2)[a]	0.2 (0.02)[c]	<0.5	0.38
Blend A	86.0 (0.1)[b] ↓	12.0 (0.1)[a]	0.5 (0.08)[b] ↑	<0.5	0.47 (0.005)
Blend B	85.2 (0.3)[b] ↓	12.0 (0.1)[a]	0.79 (0.04)[a] ↑	0.9 (0.09)	n.d.
Blend B residue	77.3 (1.1)[A]	9.6 (0.2)[A]	3.6 (0.1)[B]	n.d.	n.d.

In bracket standard deviation. Statistically significant differences ($p < 0.01$) between mean values are shown with distinct letters. Capital letters (A,B) indicate statistically significant differences between SS biocrude and Blend B residue, lower-case letters (a,b,c) indicate statistically-significant differences between MF, Blend A and Blend B.

Actual presence of biocrude in blends confirmed by:

- **Decrease of carbon content and increase in nitrogen content**, compared to MF, in both blends (A and B)
- ANOVA analysis (**99% confidence level**): statistically-significant differences (p-value ≤ 0.01) between the values of carbon and nitrogen content of Blend A and MF

- **Complete** dissolution for blend A (10 wt% SS BC nominal content)
- **Incomplete dissolution** for Blend B (20 wt% SS BC nominal content)

↓ Carbon concentration suggests a content of 16 wt.% of biocrude (Blend B)

↑ Nitrogen concentration suggests a content of 14 wt.% of biocrude (Blend B)

Blending limit of biocrude in marine fuel → **14 – 16 wt.%**

Results – Analytical characterization

Sample	Fe (ppm)	Ca (ppm)	P (ppm)	K (ppm)	Si (ppm)	Al (ppm)
SS biocrude	716 (4)	202 (2)	196 (11)	106 (2)	90 (0.5)	41 (0.3)
Marine fuel	u.d.l.	u.d.l.	u.c.l.	u.d.l.	u.d.l.	u.d.l.
Blend A	54 (3)	27 (2)	u.c.l.	u.d.l.	14 (0.7)	9 (0.05)
Blend B	75 (0.5)	16 (2)	u.c.l	u.d.l.	u.d.l.	9 (0.1)
Blend B–residue	1048 (16)	720 (10)	531 (17)	379 (5)	232 (1)	209 (0.5)

u.c.l. = under calibration limit; u.d.l. = under detection limit; absolute standard deviation in brackets

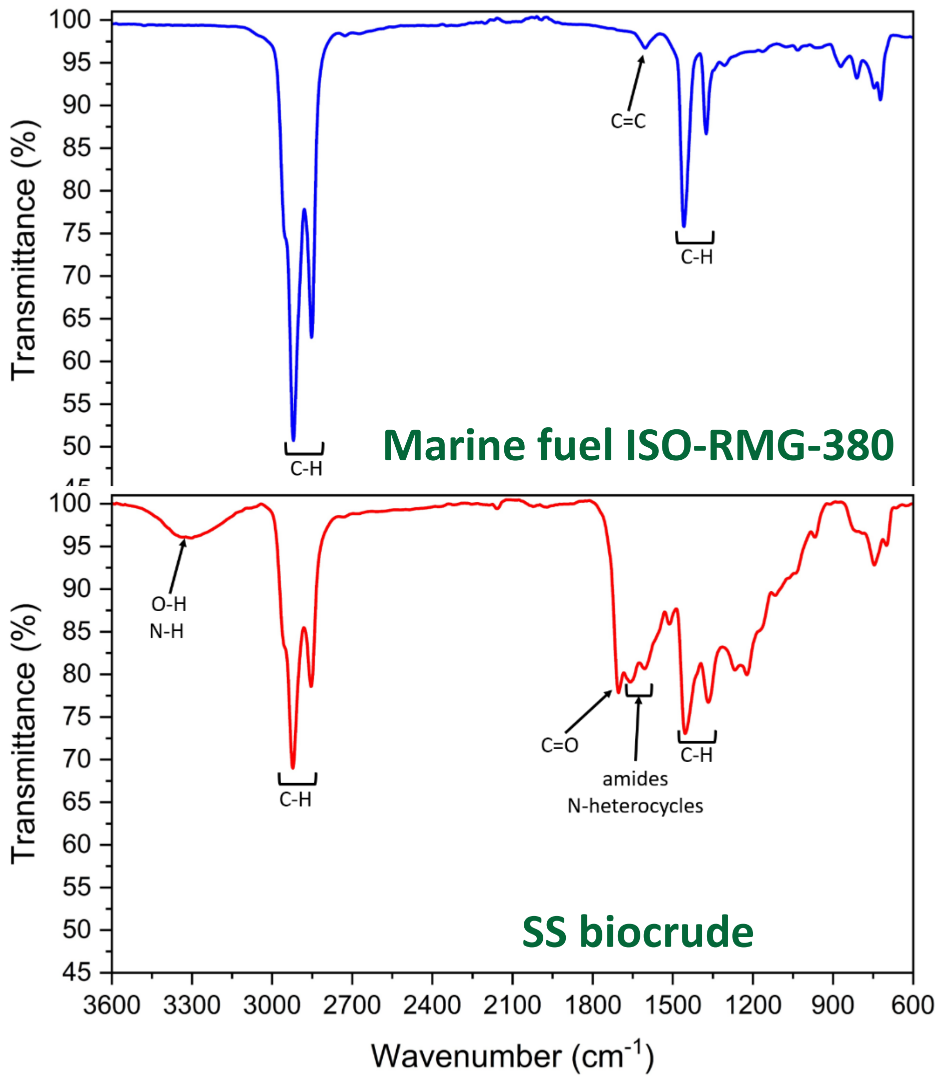
- Negligible inorganic content in MF
- Increase concentration of inorganic elements in Blend A and B comparable and unrelated to the concentration of BC

Solubility limit for each element

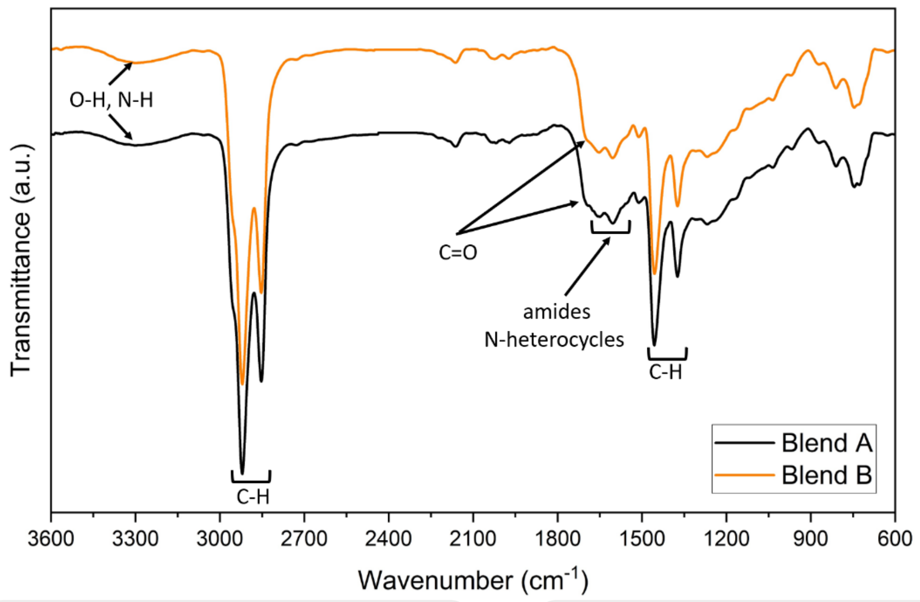
Blend B residue:

- Higher concentration of inorganics than initial biocrude
- Biocrude organics have better solubility in MF than inorganics

Results – Analytical characterization



Blend A and Blend B



Peculiar peaks of SS biocrude related to oxygenated and N-containing compounds

Blend A and B have almost identical spectra

Results - Compliance with ISO 8217 of Blend A

Shortlist of properties being considered:

- **Total acid number (TAN):** indication of amount of acidic compounds that could cause accelerated damage to engine, in particular in fuel injection equipment
- **Ash:** the formation of solid particles in the engine could cause damage to components (piston crowns, exhaust valves, turbocharger etc.)
- **Sodium and vanadium content:** higher content in ash reduces the melting temperature and these fluid ashes can adhere to the combustion chamber surface
- **Sulphur content:** high concentration in fuel increases the sulphur oxides emission
- **Aluminium plus silicon:** indication of catalytic fines in marine fuel oil; the limit of ISO 8217 ensures that the fuel treatments plants onboard reduces the catalyst fines to an acceptable level at engine inlet

	ISO-RMG-380	Limits from ISO 8217	Limit of IMO** and CIMAC[a]	Blend A	U.M.	
TAN	0.32*	<2.5		1.43	KOH/g	✓
Vanadium	6*	<350	<150	u.d.l.	mg/kg	✓
Sodium	1*	<100		u.d.l.	mg/kg	✓
Sulphur	0.38*	<0.5	<0.5	0.47 (0.005)	wt.%	✓
Ash	0.005*	<0.1		0.137 (0.05)	wt.%	✗
Aluminium plus silicon	6	<60		23	mg/kg	✓

* provided by the supplier; [a] International council con Combustion Engine; ** International Maritime Organization; u.d.l. = under detection limit; in brackets absolute standard deviation

Blend A falls in ISO 8217 limit for:

- TAN
- Sodium and vanadium content
- Sulphur content
- Aluminium plus silicon

Ash content slightly above the limit → use of RMK grade instead!

Conclusions and future works

- Analyses confirm the incorporation of biocrude aliquot in residual marine fuel:
  - Blend A and B shows identical FT-IR spectra
  - Peculiar peaks of SS biocrude related to oxygenated and N-containing compounds
- Blend A (10 wt.% nominal biocrude concentration) met basic analysed quality parameters of ISO 8217 for grade ISO-F-RMG 380:
  - TAN
  - Sodium and vanadium content
  - Sulphur content
  - Aluminium plus silicon
- The formation of agglomerates in Blend B (20 wt.% biocrude nominal concentration) suggest an incomplete blending of biocrude in the marine fuel.
- Inorganics tend to accumulate into the undissolved fraction (residue).

Direct blend of SS biocrude with residual marine fuel (ISO-F-RMG 380) without prior upgrading might provide a low-cost pathway for the inclusion of biogenic carbon

Blending limit of this specific SS biocrude in residual marine fuel between 14 – 16 wt.%

Conclusions and future works

- Selective pre-treatments to reduce inorganics content in SS briocrude
- Determination of limiting parameter(s) for SS biocrude blending in residual marine fuel
- Scale-up of blending test with larger quantity of biocrude different grades of residual marine fuel

Thanks for your attention!

The presented work is published in the OA paper:
Rizzo A.M. and Chiaramonti D., Energies, 2022, 15(2), 450. https://doi.org/10.3390/en15020450

Arturo Di Fraia[1], **Andrea Maria Rizzo [1,2]** and David Chiaramonti [1,3]

[1] *Renewable Energy Consortium for Research and Demonstration – RE-CORD, Viale Kennedy 184, 50038 Scarperia, Florence, Italy.*

[2] *DIEF, University of Florence, Department of Industrial Engineering, Viale Morgagni 40/44, Florence 50139, Italy*

[3] *Department of Energy "Galileo Ferraris", Polytechnic of Turin, I-10129 Torino, Italy*