Renewable
White paper

Renewable feedstock analyses:
Critical need for reproducibility improvements

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Throughout the regions, many ambitious targets have been set to increase renewable energy use within the transport sector[1]. As increasingly stringent legislation looks likely to be implemented, growth within renewable energy in transport is expected to be significant.

Various types of renewable feedstocks can be used to produce renewable transport fuels[2]. These include:

- Oilseed crops
- Grains and sugar crops
- Lignocellulosic biomass from agricultural residues, algae, trees, and grassess
- Biomass from waste, used cooking oils, animal fats, waste, etc.

There are mostly three types of processes to upgrade the above biomass types into renewable transportation fuels, as shown in Table 1: chemical, biological, and thermochemical[1, 2].

Legislation as a driving force
Hydrotreating of fatty acid-based feedstocks, such as vegetable oils and animal fats, is well understood[3], making it a reliable method. Feedstocks are hydrotreated in refineries all over the world. In fact, hydrotreated feedstocks accounted for 4% of the global production of renewable transport fuel in 2016[4].

However, the "food vs. fuel" debate and critical issues around land use are likely to limit the use of these types of feedstocks in the future due to additional or updated regulations.

The RED II legislation (Renewable Energy Directive for 2021–2030 in the EU) plans a phaseout of high ILUC (Indirect Land Use Change) crop-based biomass by 2030 and is promoting waste as a feedstock.

For example, the EU is also setting a maximum limit of 1.7% for processing used cooking oils and animal fats[5] into biofuel.

Therefore, it is important that more research is conducted into alternative renewable transportation fuels.

Challenges in biocrudes analyses
Pyrolysis (and especially catalytic fast pyrolysis[6] and catalytic fast hydropyrolysis[7]) is believed to be a key process of producing biocrudes that can be further hydrotreated.

Analyses of biocrudes are known to be challenging[8,9] in spite of significant efforts to establish standard methods and procedures[10,11]. Simple properties, such as elemental analysis, density, and level of contaminants, are crucial when considering hydroprocessing feedstocks. For example, contaminants, such as phosphorus, alkali metals, and alkaline earth metals, are known to trigger deactivation[12] and might cause severe plugging and pressure drops[13].

Therefore, it is important that more research is conducted into improving reproducibility.

Collaborative research
Topsoe is a world leader in processing renewable feedstocks and wanted to take on this challenge in order to create better future results.

Working with 12 other laboratories, we organized a qualitative round-robin study. Three renewable feedstocks were selected (vegetable oil, animal fat, pyrolysis oil), and the following analyses were selected:

- Elemental: C, H, N, S, O
- Physical properties: SG, cloud point, pour point, water content, total acid number (TAN)
- Contaminants: As, Al, Ca, Fe, K, Na, Mg, P, Si, Zn

The laboratories that participated in the round-robin study included the CEPSA Research Center (Spain), UT2A (University of Pau, France), and the ADNOC Refining Research Center (UAE).

Each laboratory was given a reference number. Note that Topsoe will be referred to as "Lab 1", and that the other laboratories remain anonymous..

TABLE 1
Possible conversion steps to upgrade biomass into transport fuels[1,2].

Chemical	Biological	Thermochemical
Transesterification	Conventional alcohol fermentation	Pyrolysis
Hydrotreating	Enzymatic hydrolysis and fermentation	Gasification
	Anaerobic digestion	Hydrothermal liquefaction

1. Materials and methods

1.1 Samples

Three renewable feedstocks were provided by Topsoe and shipped to all participants. The selected samples are vegetable oil (VO), animal fat (AF), and pyrolysis oil (PO). The samples were shipped between November 2017 and January 2018. The results were reported between December 2017 and April 2018.

1.2 Analytical methods

The list of standard methods used by the various laboratories is detailed in Tables 2 to 4. Note that some laboratories did not perform all the analyses, and some laboratories used several techniques to measure TAN or contaminants for example.

TABLE 2
Standard methods used for elemental analysis.

	N	S	H	O	C
Lab1	ASTM D4629	ASTM D5453/D7039	ASTM D7171	Perkin Elmer 2400 Series II analyzer	ASTM D5291
Lab2	-	ASTM D5453	ASTM D5291	-	ASTM D5291
Lab3	ASTM D5762	EN ISO 20846	-	-	-
Lab4	ASTM D5762	EN ISO 20846	ASTM D5291	ASTM D5291 (by difference)	ASTM D5291
Lab5	ASTM D4629	EN ISO 20846	ASTM D5291	-	ASTM D5291
Lab6	-	EN ISO 20846	-	-	-
Lab7	ASTM D5762	ASTM D2622	ASTM D5291	-	ASTM D5291
Lab8	ASTM D5291	ASTM D5291	ASTM D5291	ASTM D5291 (by difference)	ASTM D5291
Lab9	-	-	-	-	-
Lab10	ASTM D4629	-	-	-	-
Lab11	-	EN ISO 20846	ASTM D5291	-	-
Lab12	ASTM D4629	ASTM D5453	ASTM D5291	-	-

TABLE 3
Standard methods used for physical properties.

	SG	Cloud point	Pour point	Water	TAN
Lab1	ASTM D4052	ASTM D5773	ASTM D5949	ASTM D4928	ASTM D8045 and D664
Lab2	-	ASTM D2500	ASTM D97	Karl-Fischer	-
Lab3	-	EN 23015	ISO 3016	ASTM D6304	ASTM D664
Lab4	ASTM D4052	EN 23015	ISO 3016	ISO 8534	ISO 660
Lab5	EN ISO 12185	ASTM D2500	ASTM D97	ASTM D6304	ASTM D664
Lab6	EN ISO 12185	EN 23015	ISO 3016	ISO 12937	-
Lab7	Not disclosed	EN 23015	ASTM D5950	ISO 12937	ASTM D664
Lab8	-	-	-	ASTM E203	Modified ASTM D664 (CAN)
Lab9	-	-	-	-	-
Lab10	-	-	-	Not disclosed	ASTM D664
Lab11	-	-	-	Not disclosed	-
Lab12	-	-	-	-	-

TABLE 4
Standard methods used for contaminants.

	Contaminants
Lab1	ICP-OES (mineralization with nitric acid) and ICP-MS (dissolution in xylene)
Lab2	-
Lab3	-
Lab4	UOP 389-proc A (ICP-OES, mineralization with an acid)
Lab5	ICP-OES (VO and AF dissolved in kerosene and PO digested in nitric acid)
Lab6	-
Lab7	ISO 11885 (ICP-OES)
Lab8	ISO 11885 (ICP-OES)
Lab9	ICP-OES (solvent or mineralization with nitric acid) and ICP-MS (mineralization with nitric acid)
Lab10	ICP-OES (mineralization with nitric acid)
Lab11	-
Lab12	UOP 389-proc A (ICP-OES, mineralization with an acid)

1.3 Data treatment

Due to the characteristics of some of the samples and the low number of results in some parameters and samples, statistical data treatment was not conducted as standard round-robin studies. Therefore, one may consider this cross-check sample as a "qualitative round robin".

Median has been used as central value for all the parameters measured.

When available, standard reproducibility has been used to select outliers. When not possible to harmonize the methods of analysis, qualitative selection of outliers has been made for the evaluation of the performance.

The evaluation of the reproducibility related to the measurement of the concentration of contaminants is qualitative due to the large number of analytical methods.

The reproducibility results are shown in Table 5.

TABLE 5
Reproducibility results of the various methods.

Parameter	Reference method for reproducibility R	Calculation R
N	D4629 for vegetable oil	$R_{D4629} = 0.8194 \cdot (\text{Median})^{0.5149}$
	D5762 for animal fat and pyrolysis oil	$R_{D5762} = 0.266 \cdot \text{Median}$
S	ISO 20846	$R_{ISO20846} = 0.112 \cdot \text{Median} + 1.12$
H	D5291	$R_{D5291} = 0.2314 \cdot \sqrt{\text{Median}}$
C	D5291	$R_{D5291} = 0.018 \cdot (\text{Median} + 48.48)$
SG	ISO 12185	$R_{ISO12185} = 0.0015$
Cloud point	D2500	$R_{D2500} = 4$
Pour point	D97	$R_{D97} = 9$
TAN	D664	$R_{D664} = 0.4022 \cdot \text{Median}^{0.8199}$
Water	ISO12937	$R_{ISO12937} = 0.06877 \cdot \sqrt{\text{Median}}$

2. Results and discussion

The three renewable feedstocks – vegetable oil (VO), animal fat (AF), and pyrolysis oil (PO) – underwent a variety of analyses by Topsoe and 12 other laboratories.

Table 6 summarizes the main conclusions for the three renewable feedstocks. It was filled as follows:

- For elemental analysis and physico-chemical properties, the number of data points outside the reproducibility limits are written down.
- For contaminants, the evaluations are more qualitative. The sign "+" was given when the data were in good agreement (no deviations) or with few outliers. The sign "-" was given when significant deviation was visible.

TABLE 6
Evaluation of the results of the round-robin study.

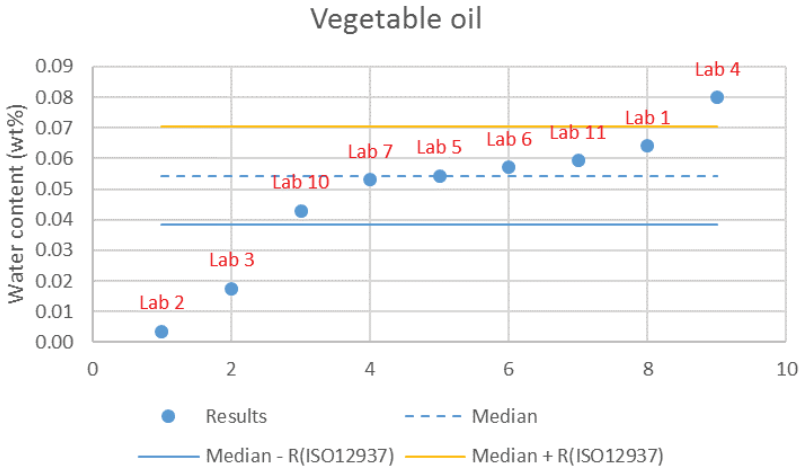
	Vegetable oil	Animal fat	Pyrolysis oil
N	1 outside repro.	0 outside repro.	outside repro.
S	1	2	4
H	1	3	2
O	Not enough measurements to conclude		
C	1	0	4
SG	1	1	1
Cloud point	0	1	N.A.
Pour point	0	0	1
Water	3	1	6
TAN	1	0	3
Al	+	+	-
Ca	+	-	-
Fe	+	-	-
K	+	-	+
Na	+	-	-
Mg	+	+	-
P	+	-	-
Si	+	+	-
Zn	+	+	-

2.1 Vegetable oil

As Table 6 (pictured above) illustrates, the sample of vegetable oil could be analyzed within reasonable accuracy by the 12 laboratories, except for water content (Figure 1) and hydrogen content (Figure 2).

Three laboratories reported water contents outside the reproducibility limit and one for H content. Note that Lab#1 used a different method (D7171 based on H NMR), and the measured H content (11.56 wt%) is quite close to the median value.

FIGURE 1
Water content measured in the sample of vegetable oil.



No major deviations were found when it came to the level of contaminants, and this is probably because of the low levels of contaminants (median values ranging between 0.1 and 1.4 wt ppm). A few outliers were present; however, due to the low concentrations, most laboratories agreed on the results. An example is given in Figure 3 for the concentration in phosphorus. Similar trends were observed for all the measured elements (As, Al, Ca, Fe, K, Na, Mg, P, Si, Zn).

FIGURE 2
H content measured in the sample of vegetable oil.

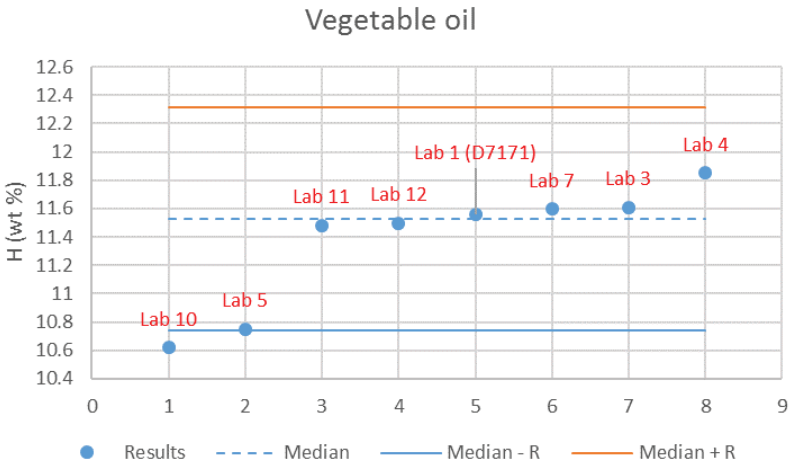
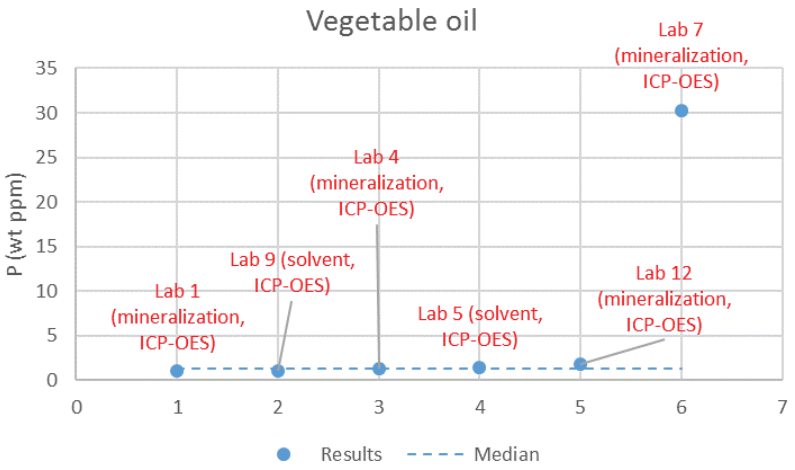


FIGURE 3
Content of phosphorus measured in the sample of vegetable oil.

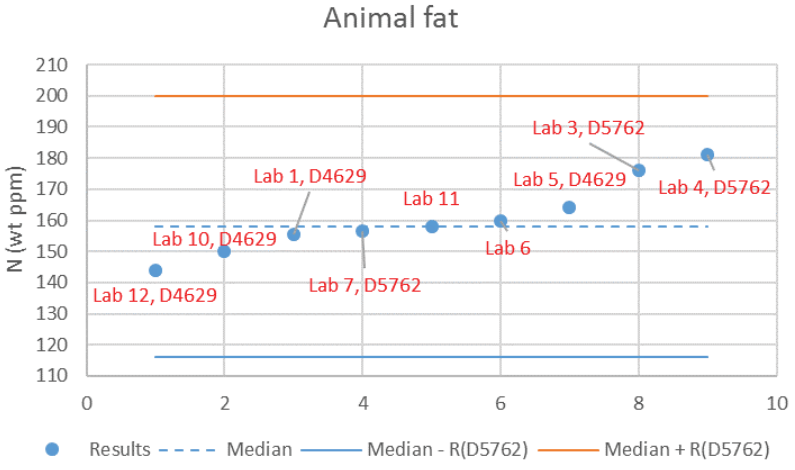


2.2 Animal fat

The picture observed for animal fat is not as elegant as that seen for vegetable oil.

When it came to elemental analysis, in addition to what was observed for the H content of the vegetable oil, nitrogen measurements also differ significantly between 145 and 180 wt ppm, although the results are within the reproducibility limit of D5762 (Figure 4). It is worth noting that the boat-inlet method (D5762) generally measures higher contents of N than the D4629 method (syringe injection), except for lab 5. One laboratory used the D5291 method; however, the values are below detection limit.

FIGURE 4
Nitrogen content measured in the sample of animal fat.



Measurement of the physico-chemical properties seemed quite consistent and reliable, except for TAN number (Figure 5). Indeed, in spite of being within the reproducibility limit, the TAN values ranged between 5 and 7 using the D664 method. Note that measurements made with D8045 and D664 by Lab#1 do not different significantly.

As for contaminants, the median values are higher than those measured for the vegetable oil (up to 87 wt ppm), and it might explain the higher deviations. The elements for which deviations were significant in the sample of animal fat are Ca, Fe, K, Na, and P. An example for P is given in Figure 6. It is striking to see a factor 2.3 between the lowest and the highest values for P content. The difference is even higher for Fe (factor 5, median value of 2.3 wt ppm), K (factor 3, median value of 14.8 wt ppm, and Na (factor 3, median value of 20.6 wt ppm).

Two methods were used for sample preparation and analysis of the aforementioned elements.

- Solvent preparation: mineralization (often in nitric acid) or dissolution in a solvent (often xylene)
- Analysis: ICP-OES or ICP-MS.

It is unclear how the sample preparation and the analytical technique affect the accuracy of the results, as seen in Figure 6 (for P) and Figure 7 (for K). However, it seems that mineralization gives higher values than dissolution in an organic solvent, which is somehow intuitive. Large deviations are anyway observed with the same sample preparation and technique, which is a critical issue.

FIGURE 5
TAN number measured in the sample of animal fat.

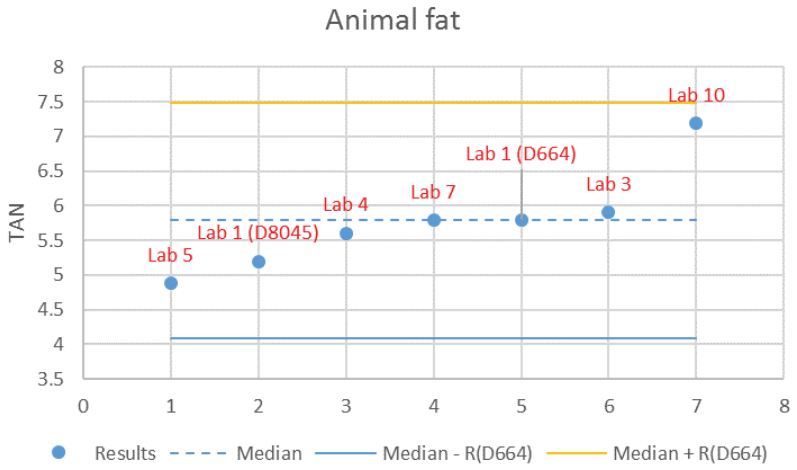


FIGURE 6
Concentration of P in the sample of animal fat.

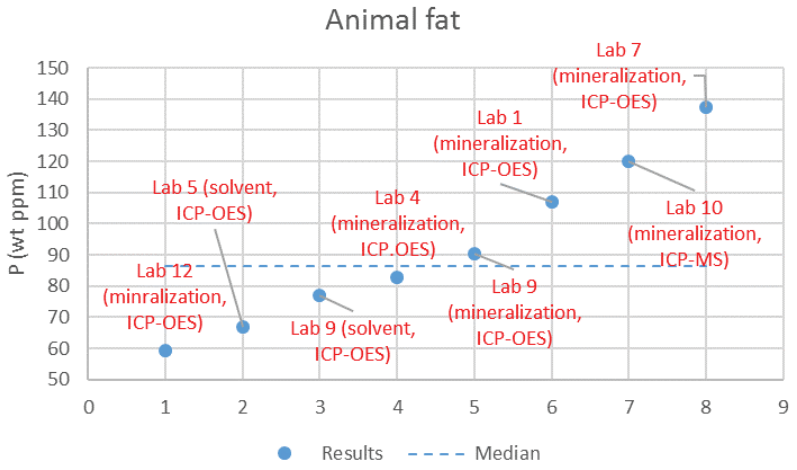
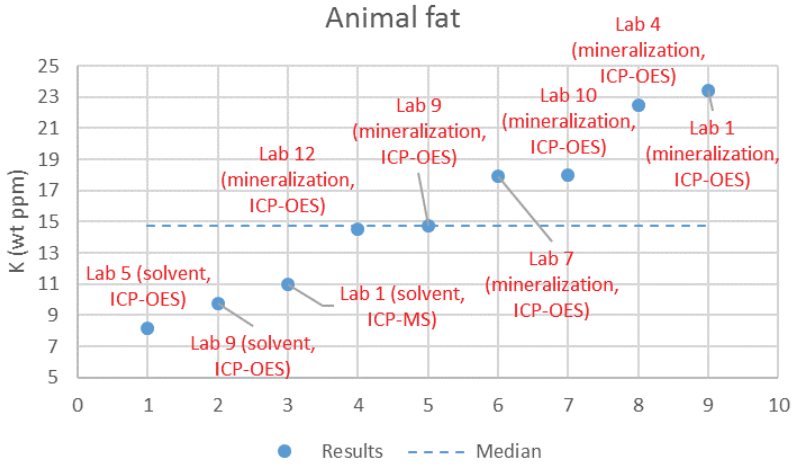


FIGURE 7
Concentration of K in the sample of animal fat.



2.3 Pyrolysis oil

Analysis of pyrolysis oil is not simple due to its biphasic nature (oil and water). In spite of the authors' efforts, there is still the possibility of not sending an identical sample of pyrolysis oil to all the participants. One additional unknown parameter is the sampling taking place in the 12 analytical laboratories. Therefore, the high discrepancies observed for the analysis of pyrolysis oil are not that surprising.

As marked in Table 6, more or less all analyses (except for SG, pour point, and K content) show significant deviations. For example, the S content varies between 52 and 78 wt ppm (Figure 8), the water content between 3 and 13 wt% (Figure 9), and the TAN number between 7 and 24 mg KOH/g (Figure 10). Similar trends were observed for contaminants (for example P content ranging between 2 and 32 wt ppm).

FIGURE 8
S content in the sample of pyrolysis oil.

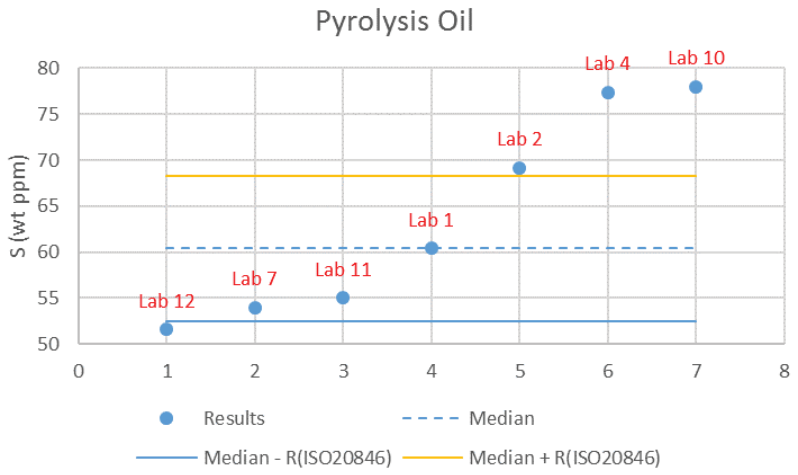


FIGURE 9
Water content in the sample of pyrolysis oil.

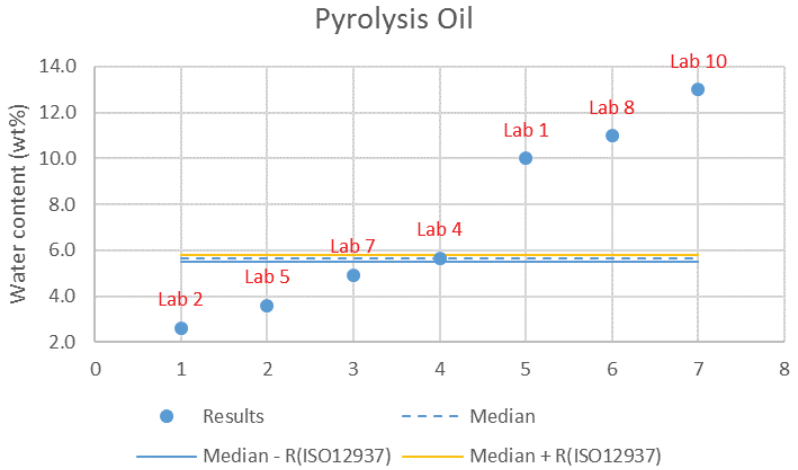
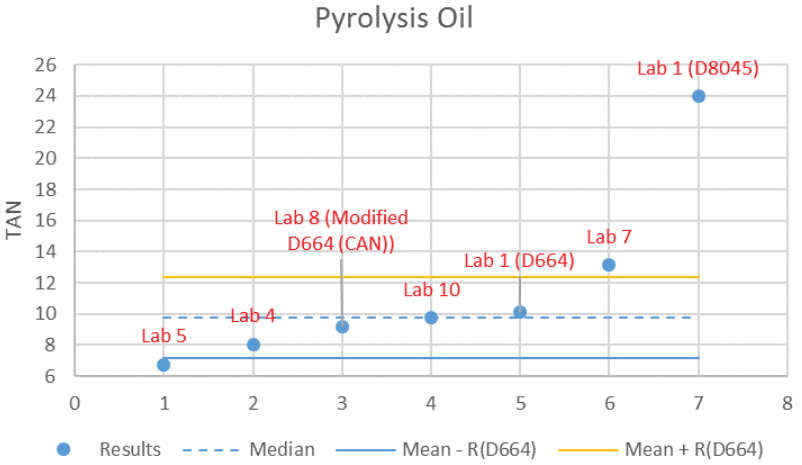


FIGURE 10
TAN number in the sample of pyrolysis oil.



3. Conclusions

This qualitative round-robin study conducted by twelve laboratories on three renewable feedstocks (vegetable oil, animal fat, pyrolysis oil) was rich in lessons. In general, good performances were observed from the laboratories for the analyses of the vegetable oil. The results were intermediate for the animal fat analyses, with remarkable deviations for N, H, and contaminants for example.

Reproducibility needs to be improved for these analyses. As for pyrolysis oil, new methods and better sample preparation need to be investigated due to the heterogeneous nature of these types of samples.

As new legislation looks set to come into place, it is critical that more research is conducted in this area. And given the research is complex and lengthy, refineries and others in the transport industry could gain from collaboration.

If you have further questions on how to get more out of your feedstocks, don't hesitate to get in touch with your local Topsoe representative.

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