19ENG09 BIOFMET

New metrological methods for biofuel materials analysis
(June 2020-May 2023)

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Production and Certification of BIOFMET Project Reference Materials

Stakeholder's Committee Meeting
30 May 2023
Alper İşleyen, TÜBİTAK UME

Partners:

Collaborators:

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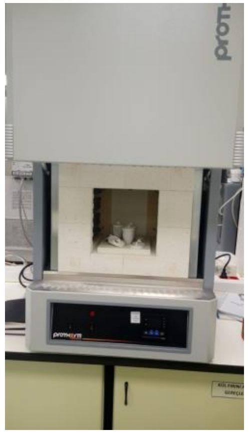
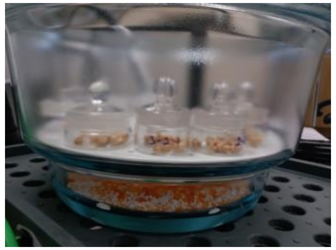
Outline

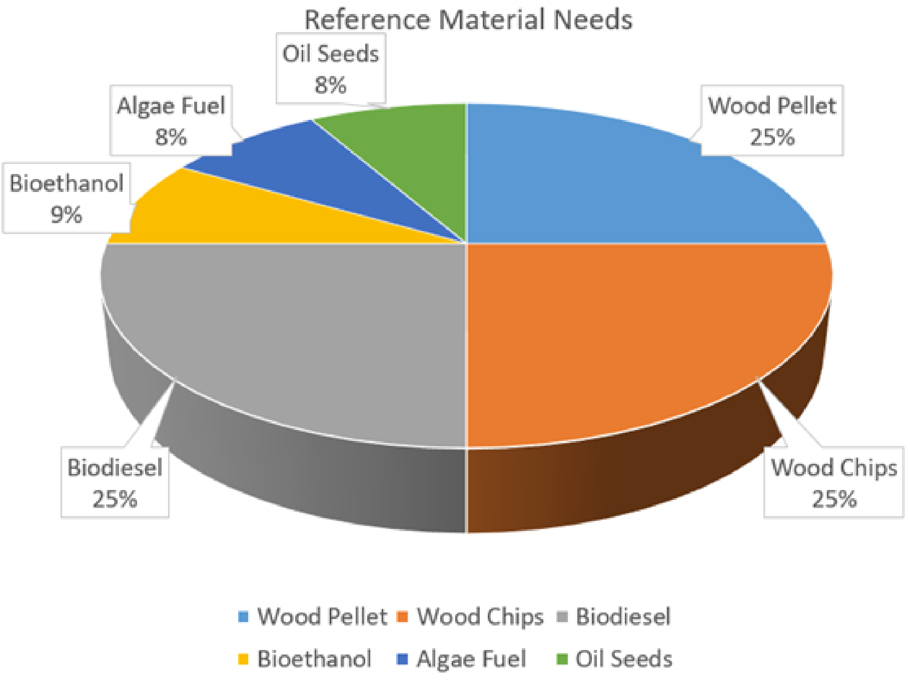
- Planning for Production of Biofuel Reference Materials
- Processing of Solid and Liquid Biofuel Reference Materials
- Homogeneity and Stability Assessments
- Characterization Strategies, Value and Uncertainty Assignment
- Comparison of Two Moisture Analysis Methods with Candidate Solid RMs
- Improvement of Ash Measurements





Survey Results for Biofuel Reference Material Needs

A questionnaire and literature survey (e.g. present CRMs, relevant standard methods) were initiated to collect information about reference material needs for solid and liquid biofuel analysis.



PARAMETERS OF INTEREST BY SURVEY PARTICIPANTS

Wood Pellet	Wood Chip	Biodiesel	Bioethanol
Gross Calorific Value	Calorific Value	**ISO EN 14214 Parameters**	**ISO EN 15376 Parameters**
Net Calorific Value	Ash	Fame Content	Ethanol + Higher Saturated Alcohols content
Ash	Moisture	Density at 15 C	Higher saturated (C3-C5) mono-alcohols content
Volatile Matter	C	Viscosity at 40 C	Methanol content
S	H	Flash Point	Water content
F	N	Cetane Number	Total Acidity
Cl	Cl	Copper Strip Corrosion (3 h at 50 C)	Electrical conductivity
H	S	Oxidation Stability (at 110C)	Inorganic chloride content
N	Heavy Metals	Acid Value	Sulfate content
O		Iodine Value	Copper content
Fixed Carbon		Linoleic acid methyl ester	Phosphorus content
Metal Oxides in Ash		Polyunsaturated (>=4 double bonds) methyl esters	Involatile material content
		Methanol content	Sulfur content
		Monoglyceride content	
		Diglyceride content	
		Triglyceride content	
		Free Glycerol	
		Total Glycerol	
		Water content	
		Total Contamination	
		Sulfated Ash content	
		Sulfur content	
		Group I Metals (Na +K)	
		Group II Metals (Ca + Mg)	
		Phosphorus Content	

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Planning for CRM Candidates Production

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UME BIOFMET CRM 01 BIODIESEL

500 mL, Amber Glass

Targetted Parameters

Parameters in EN 14214

Calorific Value
Density at 15 °C
Viscosity at 40 °C
Methanol content
Monoglyceride content
Diglyceride content
Triglyceride content
Free glycerol
Total glycerol
Water content
Sulfur, S*
Group I metals (Na+K)*
Group II metals (Ca+Mg)*
Phosphorus, P*

UME BIOFMET CRM 02 WOOD PELLET POWDER

50 g, Amber Glass

Targetted Parameters

Parameters in EN 17225-2

Calorific Value
Moisture
Ash
Nitrogen, N
Sulfur, S
Chlorine, Cl
Arsenic, As*
Cadmium, Cd
Chromium, Cr*
Copper, Cu
Lead, Pb*
Mercury, Hg*
Nickel, Ni*
Zinc, Zn

Parameters in EN ISO 16967

Aluminum, Al
Calcium, Ca
Iron, Fe
Magnessium, Mg
Phosphorus, P
Potassium, K
Silicon, Si
Sodium, Na
Titanium, Ti

Other Parameters of Interest

Carbon, C
Hydrogen, H
Manganese, Mn

UME BIOFMET CRM 03 WOOD PELLET

100 g, Amber Glass

Targetted Parameters

Parameters in EN 17225-2

Calorific Value
Moisture

*Elements selected to be spiked to reach target levels in candidate CRMs

Processing of Biodiesel CRM Candidate

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Biodiesel (B100) material
(70 x 5 L)
Source: Romania
Supplied by BRML (Romania)

0.7 µm glass fiber vacuum filtering

Combining filtered biodiesel
in 320 L HDPE container

Spiking P, K, Na, Ca, Mg
elements in mineral oil

Filling the 320 L container and
circulating the content for homogenization

Bottle filling and cap closure

Labelling and test units separation
Total: 553 units of 500 mL

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Processing of Wood Pellet Powder CRM Candidate

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Wood Pellet material
(6 x 15 kg)
Source: Poland
Supplied by DTI (Denmark)

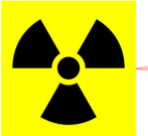
Spiking of elements to pellet
(As, Cr, Hg, Pb, Ni)

Drying spiked pellets
at 35 °C in hepa filtered
air flow oven for a week

Milling of spiked & unspiked pellets
to < 0.5 mm by cutting mill
(2 weeks)

3D homogenization
of wood powder
(80 kg, 16 hrs)

Semiautomatic filling
and capping



Gamma radiation

Labelling and test units separation
Total:1463 units of 50 g

Processing of Wood Pellet CRM Candidate

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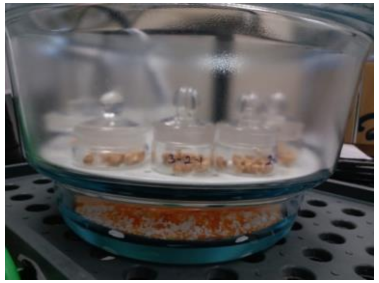
Wood Pellet material
(4 x 15 kg)
Source: Poland
Supplied by DTI (Denmark)

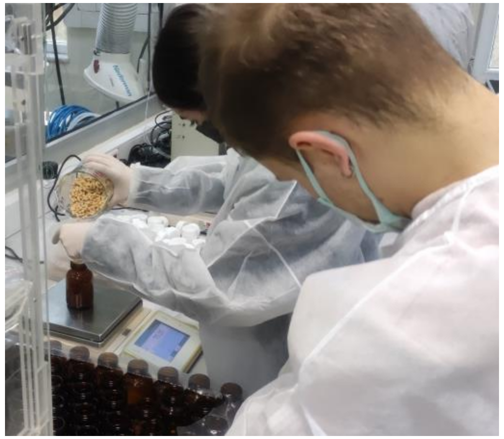


Moisture check and
selecting converging packages

Gentle homogenization
by transferring content between
120 L and 60 L HDPE containers

Splitting homogenized material
into vacuum containers

Moisture
Check



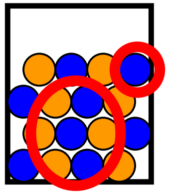
Manual filling of pellets on a
balance and capping

Gamma radiation

Labelling and test units separation
Total: 571 units of 100 g

Homogeneity

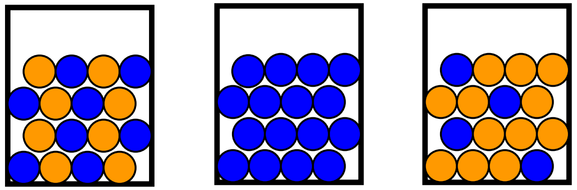
- **Within Unit Homogeneity**



✓ Heterogeneity can be eliminated by increasing minimum sample intake

✓ Important to determine the minimum amount for sample intake

- **Between Units Homogeneity**



✓ Present Heterogeneity between units can not be eliminated by increasing sample intake.

✓ Has effect on the uncertainty of the CRM.

✓ Obtained data is used to calculate the uncertainty due to heterogeneity between the units.

✓ 10 or $\sqrt[3]{total\ number\ of\ units\ produced}$ (whichever bigger) is tested.

Homogeneity Data Control

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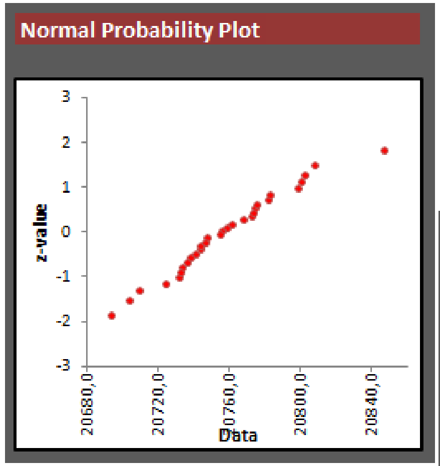
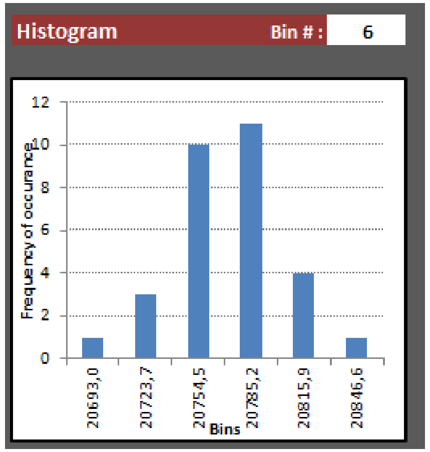
- Normal distribution investigation (Normal Probability Plots and Shapiro-Wilk Test)
- Outlier Controls (Grubbs Test)
- Unimodality (Histogram)
- Trend tests for filling order and analysis order (Linest Test)



Shapiro-Wilk Test

Alpha:	0,05
W:	9,79E-01
p-value:	7,97E-01
reject normality?	NO

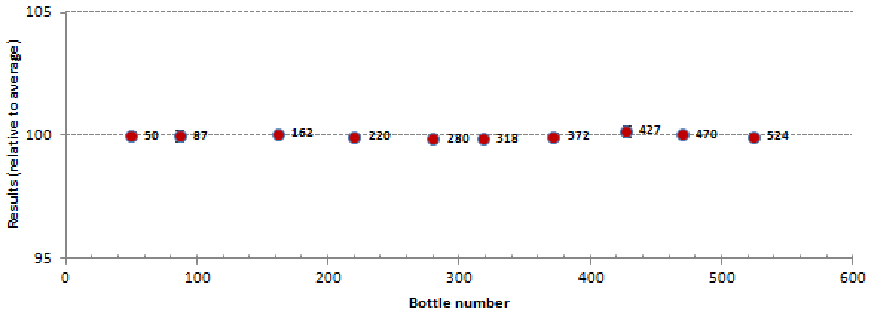
NO: normal distribution
YES: not a normal distribution

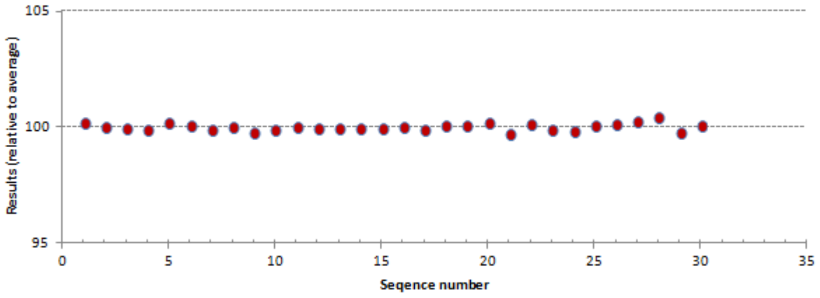


Trend Analysis

Analytical Sequence	
95%	NO TREND
99%	NO TREND

Filling Sequence	
95%	NO TREND
99%	NO TREND





Homogeneity Plots

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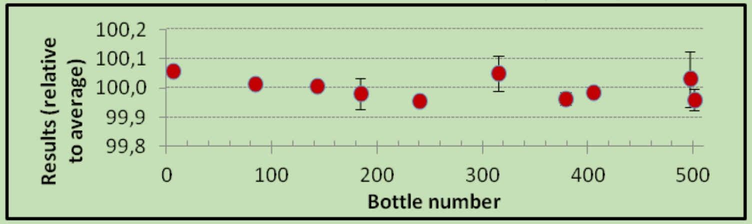
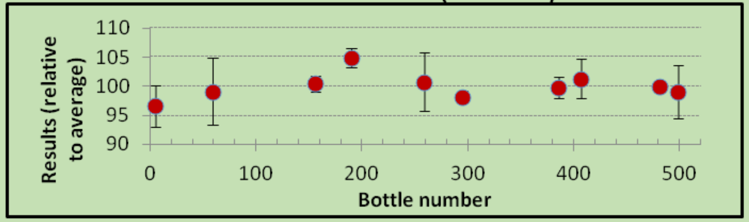
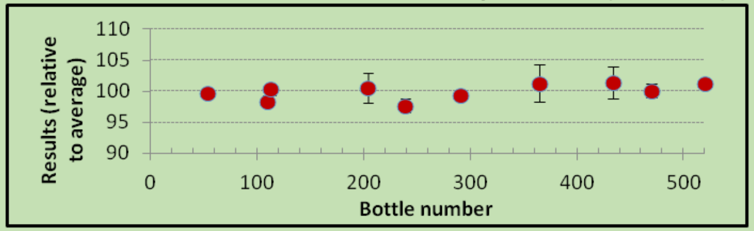
Biodiesel Calorific Value (PTB)



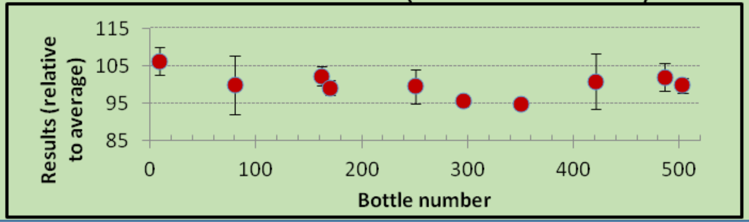
Biodiesel Sulfur (BRML)



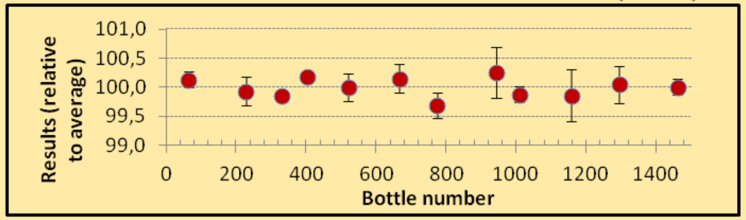
Biodiesel Linoleic Acid Methyl Ester (IMBIH)



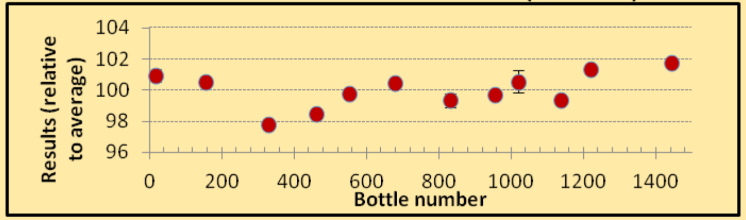
Biodiesel Methanol (TÜBİTAK UME)



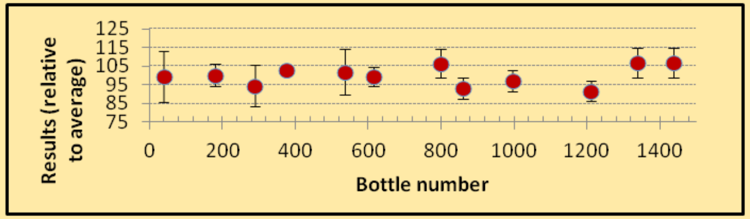
Wood Pellet Powder Calorific Value (PTB)



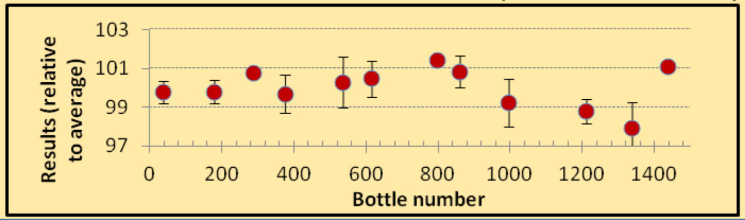
Wood Pellet Powder Sulfur (BRML)



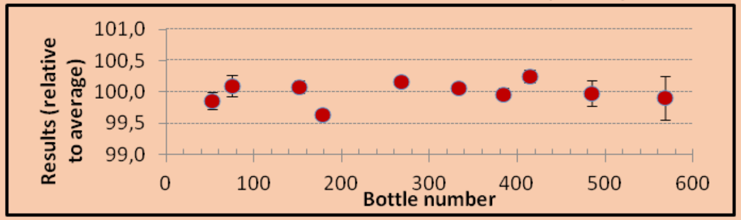
Wood Pellet Powder Ash (TÜBİTAK UME)



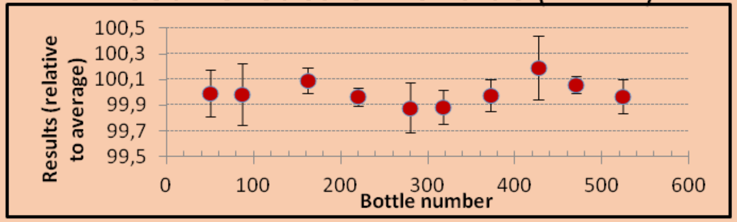
Wood Pellet Powder Moisture(TÜBİTAK UME)



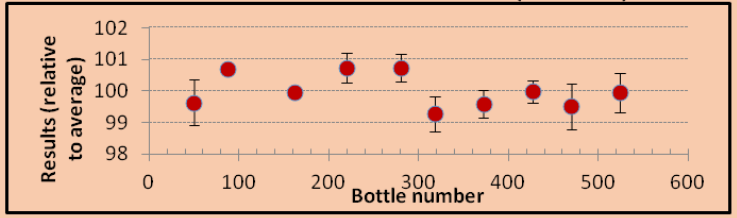
Wood Pellet Calorific Value (PTB)



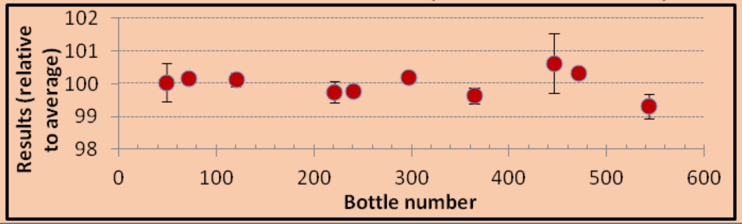
Wood Pellet Calorific Value (BRML)



Wood Pellet Moisture (BRML)



Wood Pellet Moisture(TÜBİTAK UME)



Stability Tests-Isochronous Design

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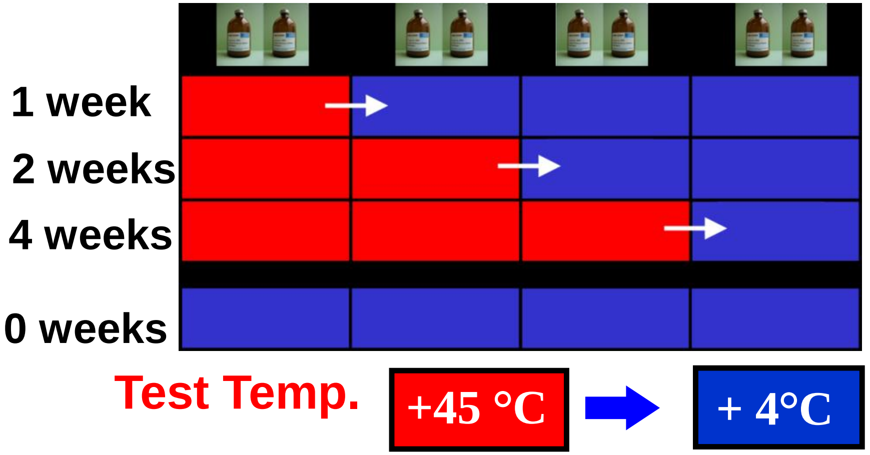
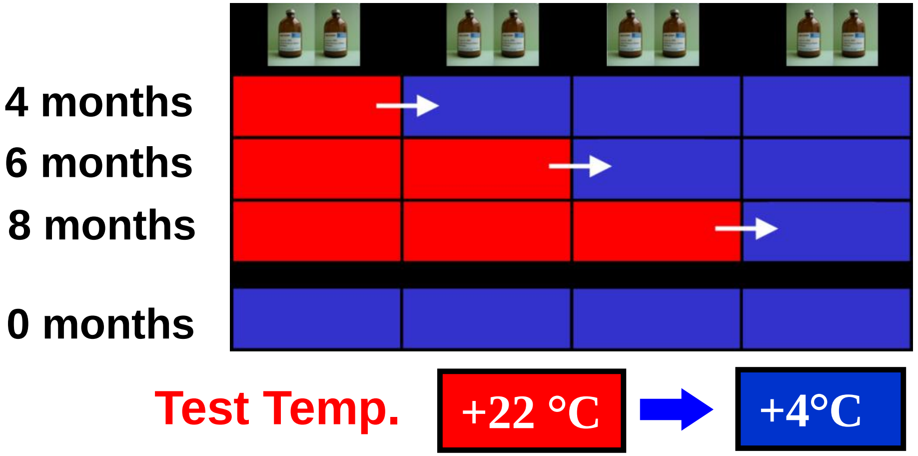
Stability during transfer → **Short Term Stability (STS)**

Stability during long term storage → **Long Term Stability (LTS)**

Isochronous Scheme





<u>Advantage of Isochronous Study:</u>
All samples are analysed the same day at the end of the study
⇨ precision is not compromised by day-to-day variation

Biodiesel Short Term Stability Plots
Homogeneity & STS Uncertainties

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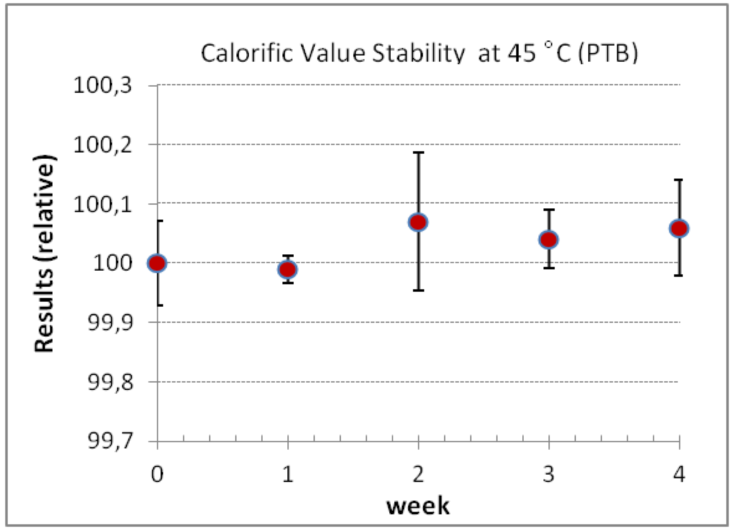

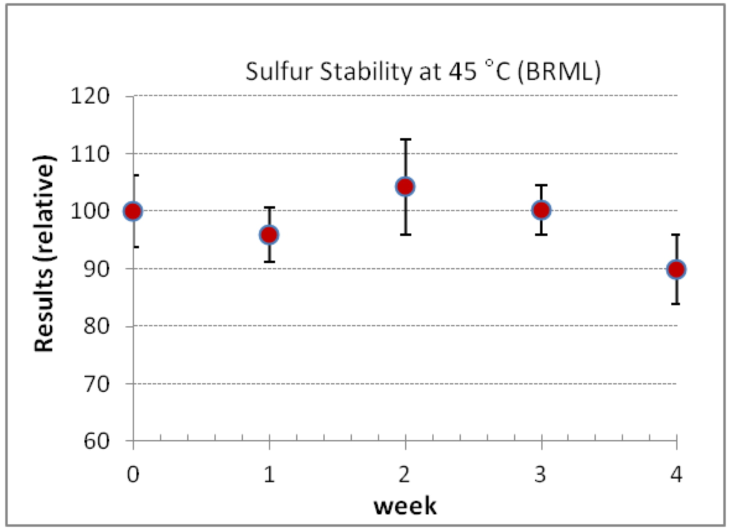

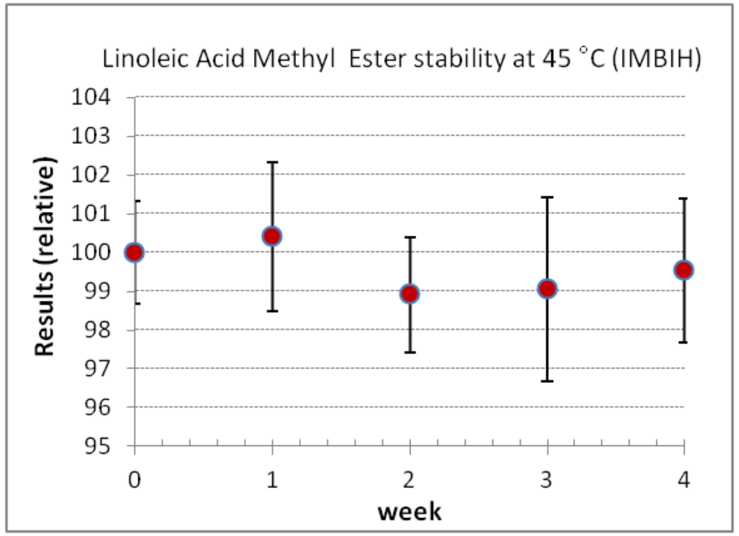

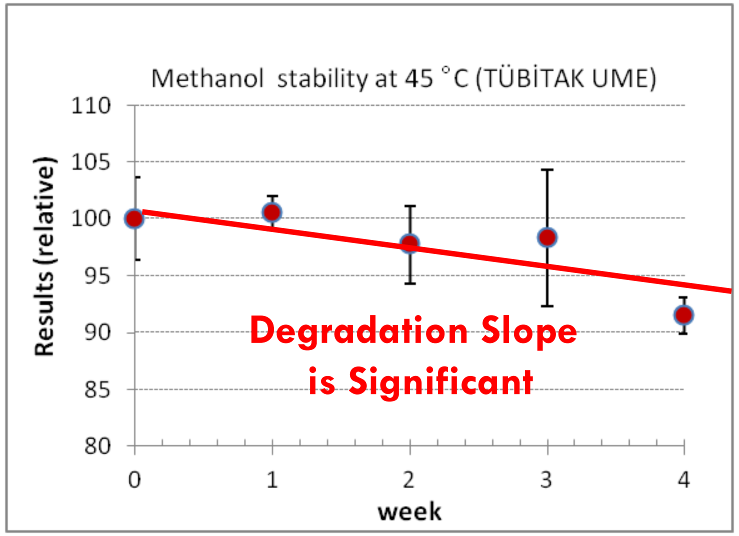

BIODIESEL		
Parameter (Lab)	Homogeneity $u_{bb,rel}$ (%)	Stability u_{STS} (%) 2 weeks 45 °C
Calorific Value (PTB)	0.023	0.023
Mono-Glycerides (BRML)	0.28	0.23
Di -Glycerides (BRML)	0.45	0.36
Tri -Glycerides (BRML)	1.2	1.1
Free Glycerol (BRML)	0.84	0.63
Total Glycerol (BRML)	0.22	0.16
Linoleic acid methyl ester (IMBIH)	0.78	0.46
Methyl palmitoleate (IMBIH)	3.0	1.5
Methyl palmitate (IMBIH)	1.7	0.69
Methyl 11-octadecenoate (IMBIH)	0.82	0.41
Methyl stearate (IMBIH)	1.5	1.4
Methyl cis-11-eicosenoate (IMBIH)	3.3	1.6
Sulfur (BRML)	1.1	1.9
Calcium (BRML)	3.8	2.8
Phosphorus (BRML)	4.2	3.2
Sodium (BRML)	8.2	4.8
Potassium (BRML)	6.3	2.8
Magnessium (BRML)	3.5	3.1
Viscosity (PTB)	0.031	0.13
Density (PTB)	0.0017	0.0029
Methanol (TÜBİTAK UME)	2.2	2.5

Wood Pellet Powder
Short Term Stability Plots
Homogeneity & STS Uncertainties

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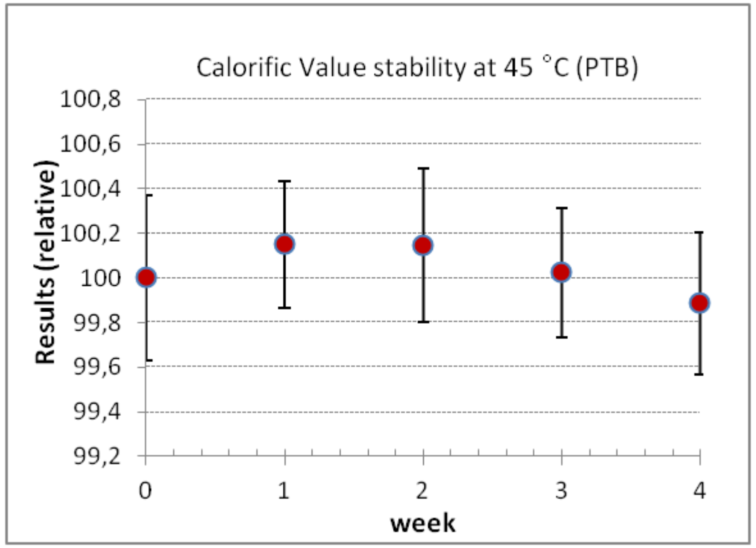

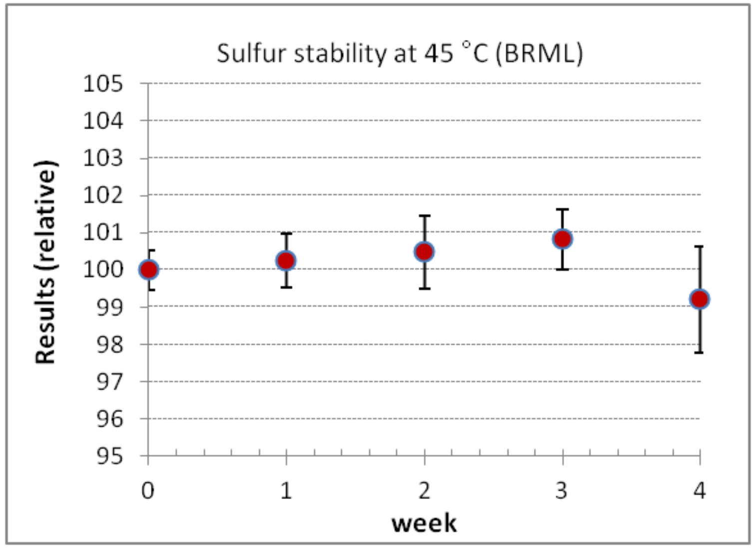

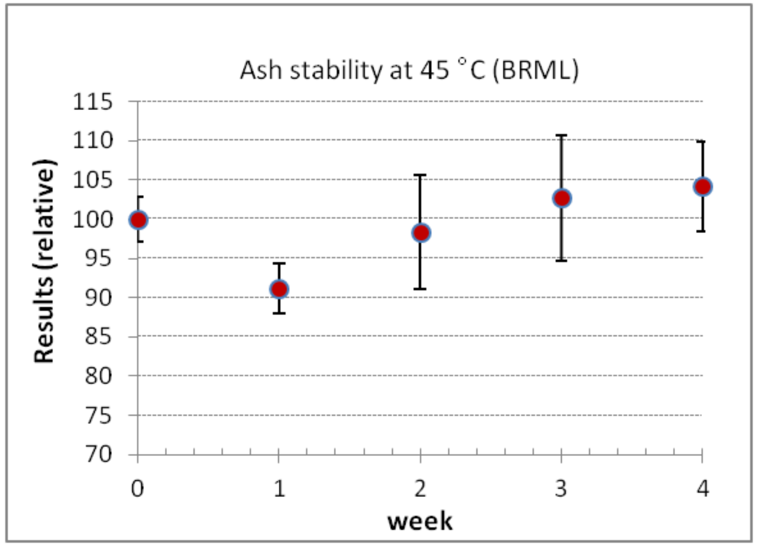

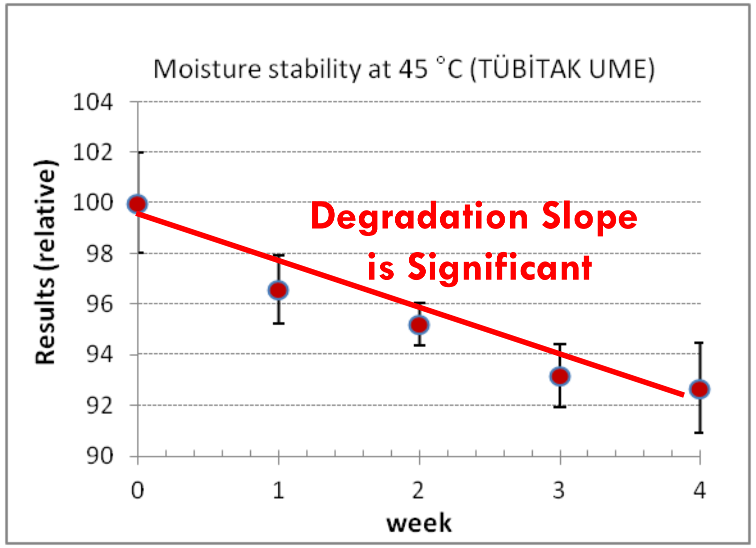

WOOD PELLET POWDER		
Parameter (Lab)	**Homogeneity $u_{bb,rel}$ (%)**	**Stability 2 weeks 45 °C u_{STS} (%)**
Calorific Value (PTB)	0.071	0.082
Moisture (TÜBİTAK UME)	0.89	2.2
Ash (TÜBİTAK UME*, BRML**)	2.5*	1.7**
Cd (BRML)	11	6.8
Cr (IMBIH)	3.1	0.56
Cu (BRML)	4.3	2.1
Ni (IMBIH)	2.4	0.82
Pb (IMBIH*, BRML**)	5.6*	2.1**
S (BRML)	1.1	0.27
Zn (IMBIH)	2.8	2.2
Ca (IMBIH)	1.5	4.5
Fe (IMBIH)	3.6	5.5
K (IMBIH)	4.4	1.7
Mg (BRML)	10	2.6
Mn (IMBIH)	1.1	0.99
Na (IMBIH*, BRML**)	7.8*	3.8**
P (BRML)	8.8	2.0
Si (IMBIH*, BRML**)	7.0*	5.0**
Ti (BRML)	8.4	1.6

Wood Pellet
Short Term Stability Plots Homogeneity, STS, LTS Uncertainties

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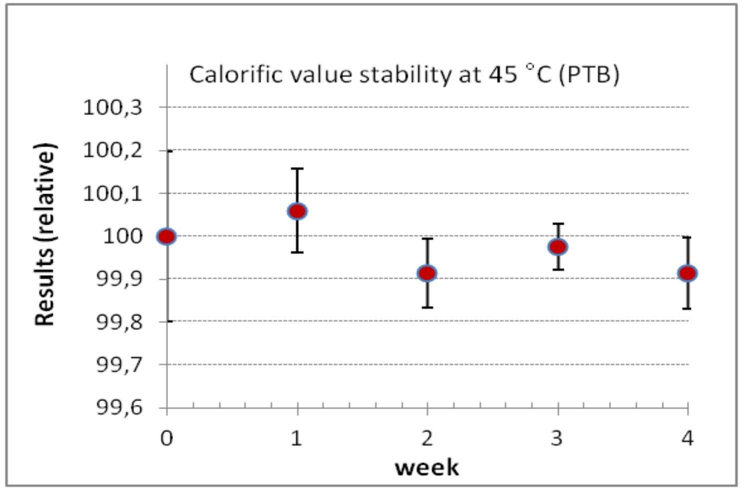

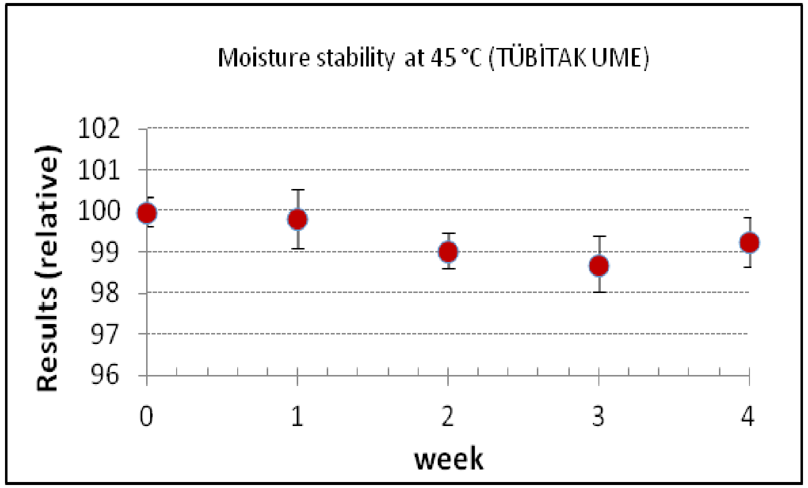

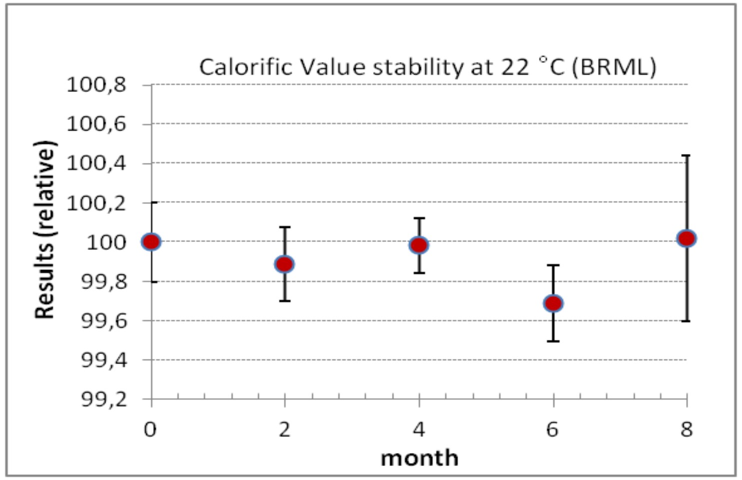

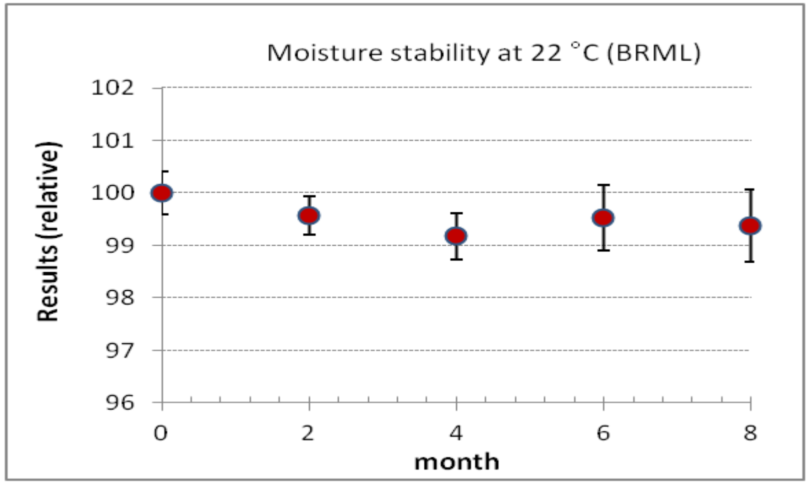

WOOD PELLET			
Parameter (Lab)	Homogeneity $u_{bb,rel}$ (%)	Stability 2 weeks 45 °C u_{STS} (%)	Stability 1 year 22 °C u_{LTS} (%)
Calorific Value (BRML*, PTB**)	0.05*	0.036**	0.22*
Moisture (TÜBİTAK UME*, BRML**)	0.25*	0.36*	0.44**

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Characterization (Value Assignment) Strategies

1. Using a **single reference** measurement procedure in a single laboratory (e.g. ID-ICP-MS method for Sulfur in Biodiesel)
2. Characterization of a **non-operationally** defined measurand using two or more methods of demonstrable accuracy in one or more **competent** laboratories (e.g. Cr in Wood Pellet by ICP-MS and MP-AES methods)
3. Characterization of an **operationally-defined** measurand using a network of competent laboratories (e.g. Moisture in wood pellet powder by ISO-18134-3:2015 method)

CRM Uncertainty

$$U_{CRM} = k \cdot \sqrt{u_{char}^2 + u_{hom}^2 + u_{sts}^2 + u_{lts}^2}$$

ISO 17034:2016, ISO GUIDE 35:2017

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Wood Pellet Moisture/Water Characterisation Study

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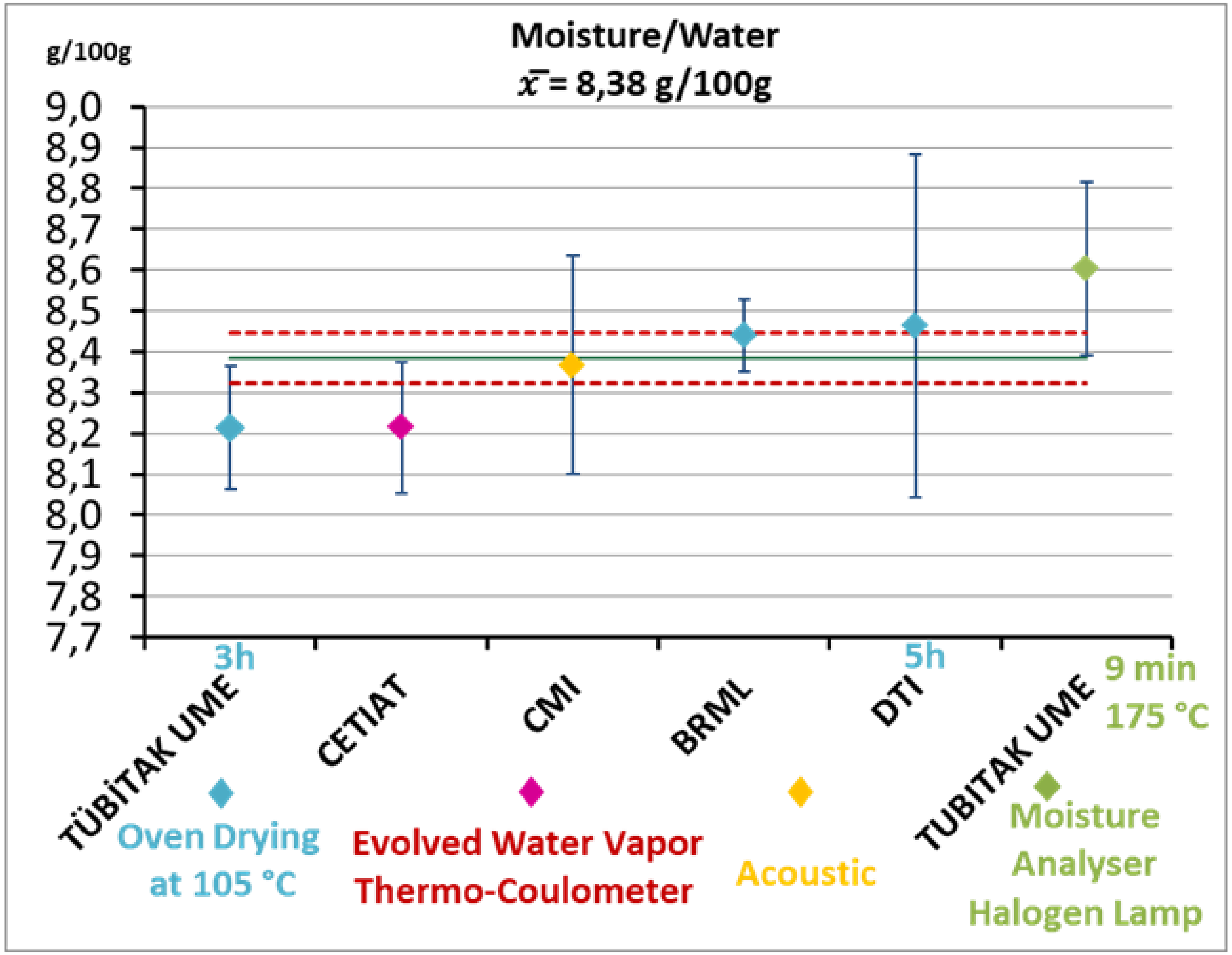

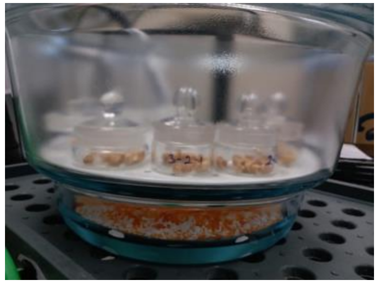

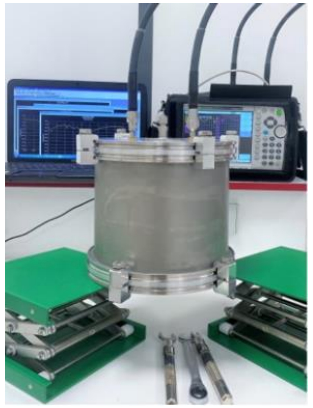

Calorific Value Characterisation Studies

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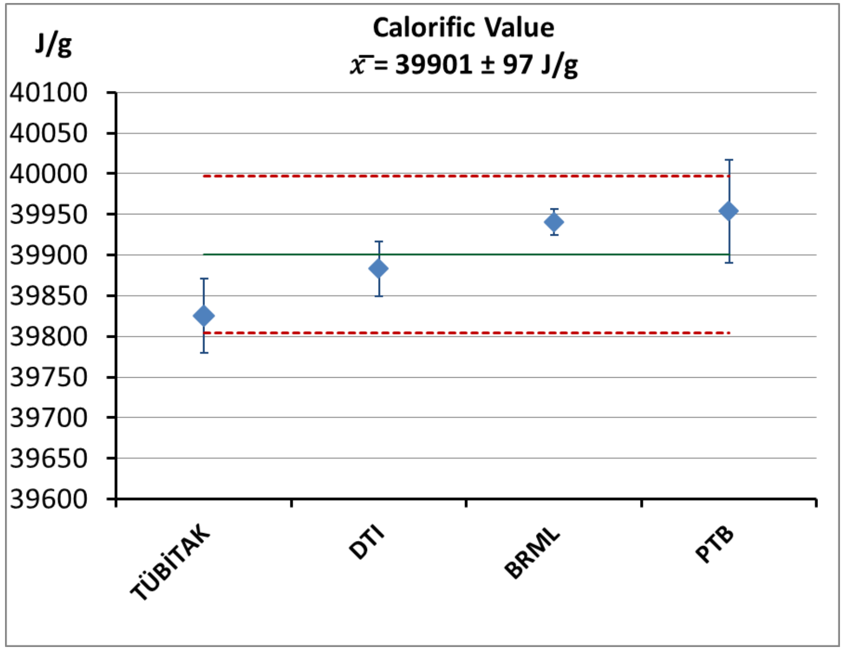
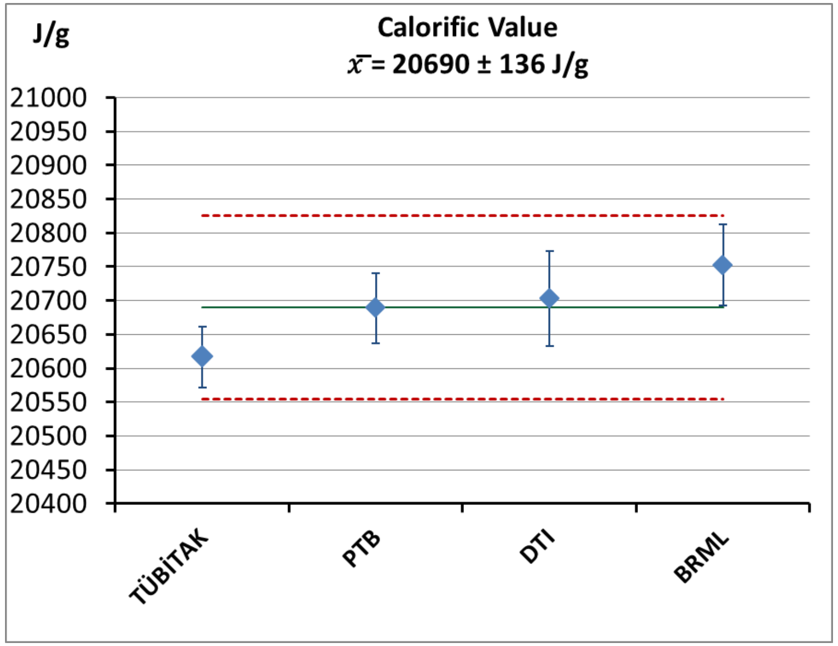
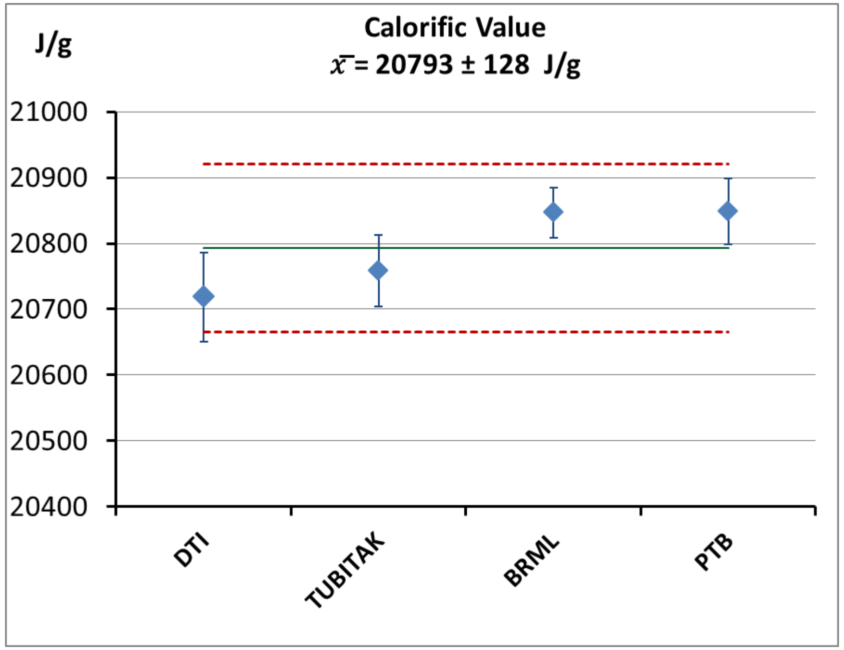
BIODIESEL



WOOD PELLET POWDER



WOOD PELLET



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Oven Drying vs Moisture Analyser

EMPIR EURAMET
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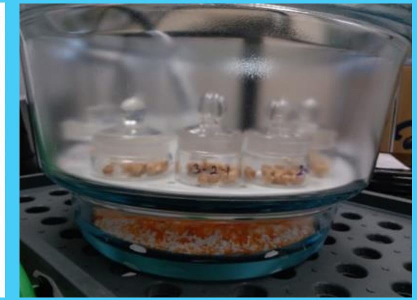

ISO-18134-3:2015 Method, Temperature: **105 °C**
Sample Heating Time: **3-5 hours**
Time needed for 36 Measurements : **7- 8 hours**
Total Number of Weighings: **108-180**
Total Number of weighing bottles: **36**
Requires: dessicator with dessicant

Wood Pellet Pow: u_{hom} (%): **0.89**, u_{STS} (%): **2.2**

Wood Pellet u_{hom} (%): **0.25**, u_{STS} (%): **0.36**


Temperature: **105 °C:** pellet powder, **175 °C** : pellet
Sample Heating Time: **3 min**-powder, **8 min** for pellet
Total Time needed for 36 Measurements : **3h/6h**
Total Number of Weighings: **36**
Total Number of aluminum weighing plates: **2**
No dessicator with dessicant is required

Wood Pellet Powder: u_{hom} (%): **0.65**, u_{STS} (%): **1.4**

Wood Pellet : u_{hom} (%): **0.55**, u_{STS} (%): **0.20**

Ash Measurements

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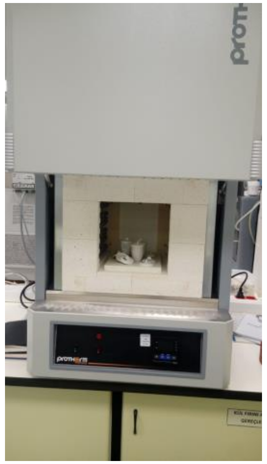
ISO 18122:2022
Defines use of a balance capable of reading to the nearest **0.1 mg**



Balance with 0.1 mg Readability

	Bottle No	Weight Empty bottle (g)	Weight Empty bottle + Sample (g)	Weight after Ashing (g)	Ash Content[Wet] (g/100g)
1	39-1	28,8251	29,7935	28,8265	0,145
2	180-1	30,1776	31,1082	30,1792	0,172
3	289-1	30,2975	31,2354	30,2990	0,160
4	376-1	31,4041	32,354	31,4063	0,232
5	536-1	30,3882	31,3377	30,3901	0,200
6	615-1	30,5544	31,4719	30,5557	0,142
7	799-1	30,9556	31,9901	30,9575	0,184
8	860-1	30,8452	31,7919	30,8474	0,232
9	996-1	28,9917	29,9868	28,9941	0,241
10	1211-1	28,3408	29,285	28,3433	0,265
11	1338-1	31,0568	31,9895	31,0590	0,236
12	1437-1	30,8627	31,8441	30,8649	0,224
13	39-2	28,991	30,038	28,9930	0,191
14	180-2	30,862	31,8884	30,8634	0,136
15	289-2	30,5537	31,5922	30,5541	0,039
16	376-2	30,3876	31,3916	30,3888	0,120
17	536-2	28,3405	29,4019	28,3422	0,160
18	615-2	31,0576	32,0896	31,0581	0,048
19	799-2	30,1771	31,2403	30,1796	0,235
20	860-2	31,405	32,4303	31,4058	0,078
21	996-2	28,8245	29,831	28,8264	0,189
22	1211-2	30,8444	31,9999	30,8473	0,251
23	1338-2	30,9544	32,0149	30,9571	0,255
24	1437-2	30,2976	31,3364	30,3001	0,241

Avg	0,182	g/100g
SD	0,065	g/100g
RSD	**35,5**	**%**

Balance with 0.01 mg Readability

	Bottle No	Weight Empty bottle (g)	Weight Empty bottle + Sample (g)	Weight after Ashing (g)	Ash Content[Wet] (g/100g)
1	39-1	31,05674	32,51881	31,06019	0,236
2	180-1	31,40455	32,85538	31,40780	0,224
3	289-1	30,86251	32,31448	30,86572	0,221
4	376-1	28,34106	29,79704	28,34455	0,240
5	536-1	30,55297	32,00488	30,55652	0,245
6	615-1	30,29754	31,75746	30,30095	0,234
7	799-1	30,95462	32,41181	30,95830	0,253
8	860-1	30,84532	32,30066	30,84850	0,219
9	996-1	28,99206	30,44316	28,99520	0,216
10	1211-1	28,8249	30,2739	28,82820	0,228
11	1338-1	30,38783	31,84003	30,39122	0,233
12	1437-1	30,1776	31,62817	30,18132	0,256
13	39-2	31,40414	32,8573	31,40707	0,202
14	180-2	30,8443	32,2957	30,84777	0,239
15	289-2	28,99155	30,44392	28,99451	0,204
16	376-2	31,05622	32,50509	31,05921	0,206
17	536-2	30,86194	32,32111	30,86538	0,236
18	615-2	30,17735	31,6304	30,18041	0,211
19	799-2	28,34089	29,7997	28,34444	0,243
20	860-2	30,55285	32,00395	30,55650	0,252
21	996-2	30,29676	31,75162	30,30060	0,264
22	1211-2	30,95454	32,40752	30,95764	0,213
23	1338-2	28,82443	30,28181	28,82813	0,254
24	1437-2	30,38738	31,84337	30,39121	0,263

Avg	0,233	g/100g
SD	0,019	g/100g
RSD	**8,0**	**%**

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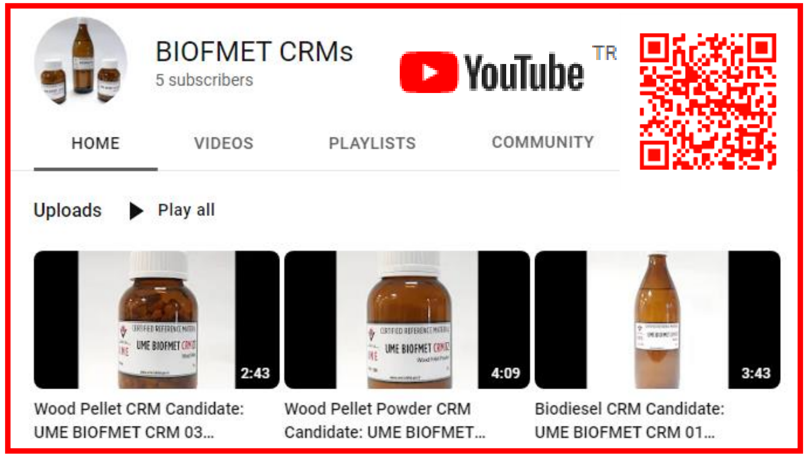


TÜBİTAK UME BIOFMET project RM processing team

Acknowledgment

- EURAMET EMPIR Programme
- Project Partners & Collaborators

- <u>TÜBİTAK UME Staff:</u>

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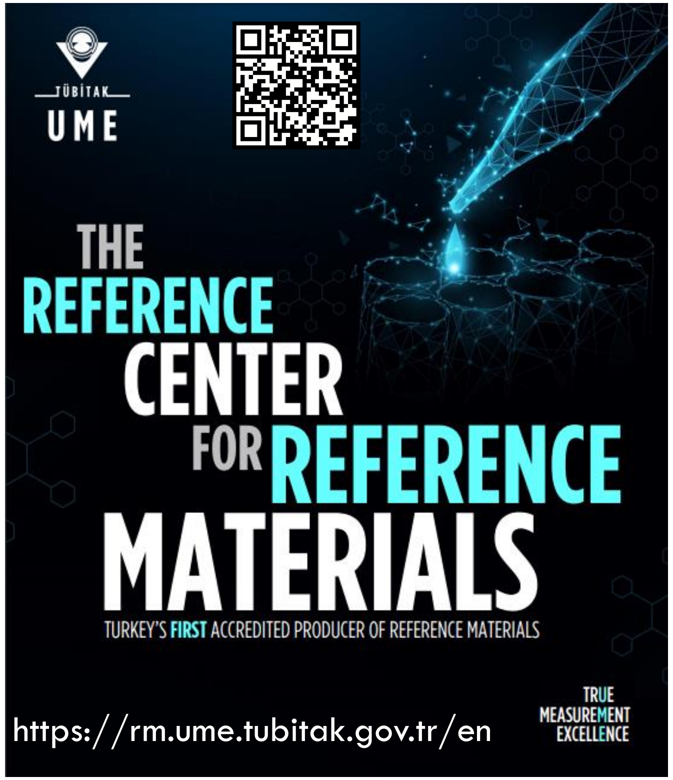
Murat Tunç, Fatma Gonca Coşkun (Inorganic Impurity Measurements)
Hasibe Yılmaz (Methanol Measurements)
Adnan Şimşek (C,H,N Measurements)
Gökhan Aktaş, Hatice Altuntaş (Processing & Stability Tests)
Tülin Erdoğan (Ash & Ion Measurements)
Uğur Akkaya (Project Logo Design)

- TUBITAK BIDEB 2247-C Intern Researcher Scholarship Program (STAR)
- <u>Scholar and Intern Students:</u>

Berke Can, Elif Nur Kırbaş, Beyzanur Çobanoğlu, Rana Yaldız, Hikmet Küçük, Ayşenur Düzgün, Feyzanur Şentürk, Muhammed Faruk Kıran, Selina Turunç



Thank you for your attention!

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