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Production of Solid Sustainable Energy Carriers from Biomass by Means of Torrefaction

Deliverable No. 8.2 Requirements for a MSDS for torrefied material

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1 Summary

This report describes the development of a material safety data sheet (MSDS) for torrefied material as fuel. It aims to highlight existing gaps in the knowledge about torrefied material. Companies can use the template, but will have to modify it according to their own specific product. It shall ensure a safe and secure handling of torrefied biomass on the market.

2 Description of deliverable no. 8.2

Chemicals are generally to be produced and used in such a way that negative effects on the human and the environment remain as low as possible. For a long time data concerning health- and environmental effects of chemicals were not available for 95% of the products on the market. The EU's declared objective was to improve the level of knowledge about dangers and risks that chemicals may pose. Therefore, the European regulation EC No. 1907/2006 concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) has been developed. According to the first preliminary remark "the regulation should ensure a high level of protection of human health and the environment, as well as the free movement of substances, on their own, in preparations and in articles, while enhancing competitiveness and innovation. This Regulation should also promote the development of alternative methods for the assessment of hazards of substances."

The EU Regulation centralizes and simplifies legislation for chemicals throughout Europe and entered into force on 1st of June 2007. Companies are expected to assume more responsibility for the safe use of their products, according to the motto: „No data – no market“. The central communication document between market actors should be the MSDS.

Whether registration under REACH for torrefied material is required, cannot be unequivocally determined at the present. On the one hand the feedstock, solid biomass either from lignocellulose plants, or from agriculture residues, requires it. By going through a heat treatment in an oxygen deficient environment, the resulting product is comparable to coal, which is also not under the obligation to register and covered by the regulation in Annex V/7.

On the other hand the heat treatment can be seen as a chemical treatment (see Article 3/39) because torrefaction is a thermo-chemical production process which changes the natural occurring substance as such (see Article 3/40) by solving water, hemicelluloses and further volatiles out of it and leads to a product with porous fine particle structure.

During torrefaction numerous reaction products are formed. Their yield strongly depends on the torrefaction conditions (e. g. temperature, pressure and time) and on the biomass properties so that general valid values cannot be specified. The following figure gives an overview of the expected process products. Classifications are based on state at room temperature, which can be solid, liquid or gaseous.

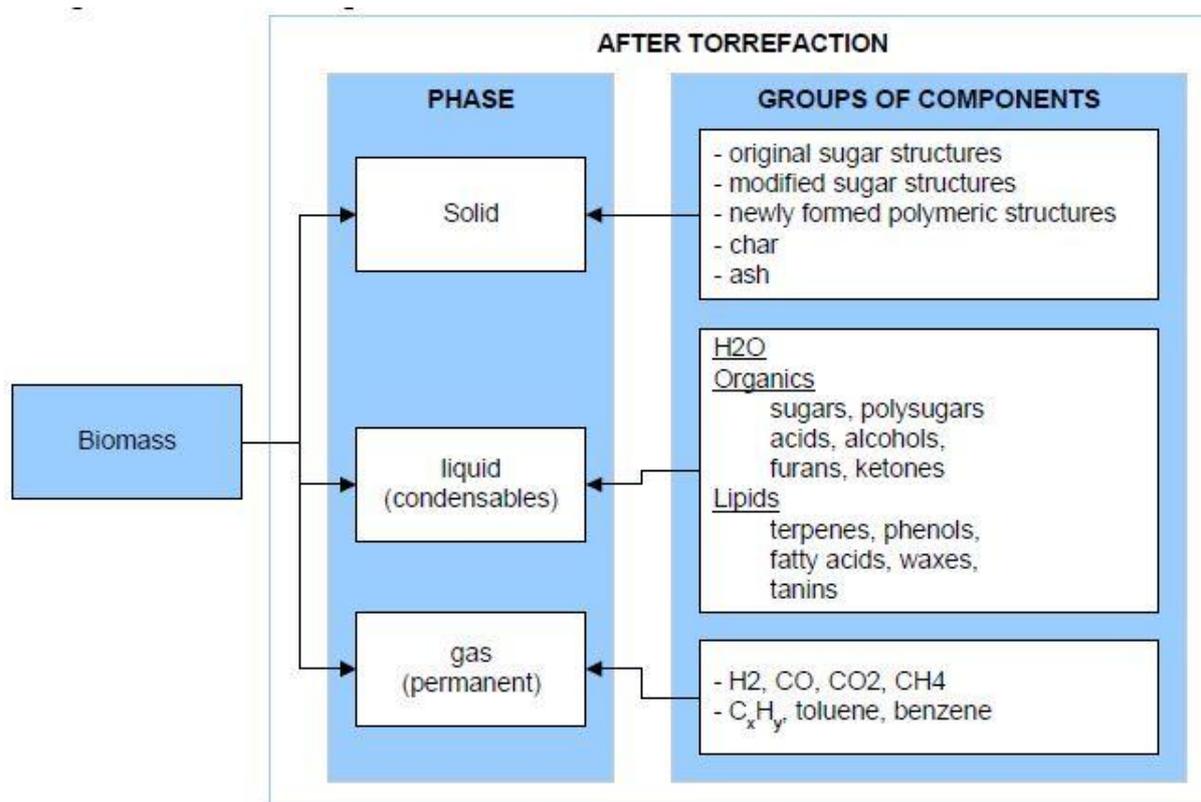


Figure 1: Products formed during torrefaction of biomass (source: Bergmann 2005)

The solid phase consists of besides the main product a random structure of the original feedstock's sugar structures and reaction products. The reaction products that remains solid are large modified sugar structures, newly formed polymeric structures with possibly a certain degree of aromatic rings, typical carbon rich char structures and the ash fraction. The liquids can be divided into sub-groups. One sub-group is reaction water as a product from the thermal decomposition, in addition to the freely bound water that has been released from the biomass by evaporation. The organic sub-group consists of organics that are mainly produced during devolatilisation and carbonization. Lipids are a group of compounds that are present in the original biomass. They are not really reaction products, but inert compounds that may evaporate under torrefaction conditions. This sub-group contains compounds such as waxes and fatty acids. Although these compounds are mainly liquids, some can be solid at room temperature. The gas phase includes the gases that are to be considered permanent gases. In general, these are compounds with a boiling point below -33°C , but also light aromatic components such as benzene and toluene. It must be emphasized that the yields and types of products are strongly dependent on the torrefaction conditions and the biomass properties (Bergmann et. al. 2005). Gas and condensables occur during the process and are mainly solved from the main product of torrefied biomass.

3 Content of Material Safety Data Sheet Template

A MSDS should ensure a free trade between countries and business partners. Currently torrefied material does not have a safety classification under International Maritime Organization (IMO) and cannot be transported by ocean vessels without special permission since the product has similarities with charcoal, which is prohibited to be transported in bulk (IEA Task 32, 2012). In the following the information given in this MSDS-template for torrefied biomass refers to the EU regulation EU 1907/2006. Section titles are given in § 31 and Annex II of the regulation. Explanatory notes to the sub-items are in the Commission Regulation (EU) No. 453/2010. The present document provides a template for a specific MSDS which has to be modified to the users' product properties. Thus, special attention is given to parts that are marked in *italics*. Additionally to the MSDS often a chemical analysis of the product composition (including all contained substance or mixture) is a pre-condition to most of the REACH processes. Note the legal advice in Section 16 too.



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Material Safety Data Sheet for Torrefied Biomass	Author: SECTOR Project Date of preparation: January 2013 Version: 1.0 Page:1/10
According to EC No. 1907/2006 (REACH)	

SECTION 1— IDENTIFICATION OF CHEMICAL SUBSTANCE / PREPARATION AND COMPANY

1.1 Identification of the substance or preparation

Product Identifier: Carbon [C]

CAS-Number: 744-44-085 [C]

Product name: torrefied biomass, torrefied lignocellulosic biomass, torrefied wood *in form of chips, powder, pellets or briquettes*

Synonyms: biocoal, torrefied pellets

Product description: Biomass *in the form of chips*, are thermally treated in an oxygen deficient environment, which leads to a dry product. Torrefaction combined with densification leads to an energy-dense fuel carrier.

Appearance: Depending on feedstock and torrefaction process, the colour of the treated biomass can vary from brownish to black. *For transport and handling reasons it is common to densify it to pellets or briquettes.*

REACH Registration Code: *not existent yet*

1.2 Product use

Biofuel for conversion to energy in power plants and substitution material for co-firing in coal fired power plants.

1.3 Manufacturer's and/or supplier's name

Street Address: *postal address*

City: *city*

Postal Code: *postal code*

Province:

Non-Emergency assistance: *contact person, phone number, office hours*

1.4 Emergency telephone

Emergency Contact: *phone number, name, office hours*

Official advisory body: *national health security number*

SECTION 2 — HAZARDS IDENTIFICATION

According to the legislation of the European Union, torrefied biomass for energetic use is not been classified yet. However, it is classified as Material Hazardous in Bulk (MHB) by the International Maritime Organization (IMO). Due to the normal biodegradation of biomass torrefied biomass material emits gaseous substances such as carbon-monoxide, carbon-dioxide and small amounts of methane and hydrogen in combination with oxygen depletion. The material shall be handled only by trained personnel and with the necessary care.

2.1 Fire and Explosive Risk

- Flammable/combustible material, classified as ADR 4.2
- May be ignited by friction, heat, sparks or flames
- May burn rapidly with flare burning effect
- Highly explosive dust may be generated during handling
- Powders, dusts or shavings, may explode or burn with explosive violence
- May re-ignite after fire is extinguished
- When pneumatically transported, static discharge may occur

2.2 Health

- Fire may produce irritating and/or toxic gases
- Contact may cause burns to skin and eyes
- Runoff from fire control may cause pollution

2.3 Low Oxygen Risk

- Ventilate space where torrefied material is stored before entry
- Always measure both carbon monoxide and oxygen content before entry in space where torrefied wood is stored
- Entry of personnel into cargo and adjacent confined spaces shall not be permitted until tests have been carried out and it has been established that the oxygen content and carbon monoxide levels have been restored to the following levels:
 - oxygen 20.7% and
 - carbon monoxide <100 ppm.

If these conditions are not met, additional ventilation shall be applied to the cargo hold or adjacent confined spaces and re-measuring shall be conducted after a suitable interval.

- An oxygen and carbon monoxide meter shall be worn and activated by all crew when entering cargo and adjacent enclosed spaces.

2.4 Potential Health Effects

- Skin: May cause irritations to the skin (Redness, scaling, itching)
- Eyes: May cause irritations to the eyes (tearing, burning)
- Ingestion: May cause gastrointestinal irritations
- Inhalation: May cause irritations to the respiratory system (Irritation to the lungs and mucous membrane)

2.5 Chronic effects

- Heat treated wood is not tested yet and therefore not listed by NTP, IARC or regulated as a carcinogen by OSHA

2.6 Toxicity of leachate

- Only the volatile organic constituents are partly soluble in water.

SECTION 3 — COMPOSITION/INFORMATION ON INGREDIENTS

Product composition is woody or cellulosed fibered biomass. The composition varies depending on the; feedstock used, torrefaction technique and torrefaction conditions (e.g. time and heat). During torrefaction the biomass loses most of the low energy contents of the material and three primary products are produced:

- a) solid products (*modified sugar structures, newly formed polymeric structures*)
- b) condensable liquids (*moisture, acetic acid and other oxygenates*)
- c) non-condensable gases (*CO₂, CO and small amounts of methane*)

These products must be determined by the producer of torrefied material.

SECTION 4 — FIRST AID MEASURES

General

- Ensure that medical personnel are aware of the material(s) involved and take precautions to protect themselves.

Eye Contact

- Flush eyes with running water for at least 20 minutes.

Skin Contact

- Flush skin with running water.
- Wash clothing before reuse.

Ingestion

- Wash mouth with distilled or clean/drinking water.
- Get medical aid.

Inhalation

- Move victim to fresh air and call emergency medical service.
- Give artificial respiration if victim is not breathing.
- Administer oxygen if breathing is difficult.
- Keep victim warm and quiet.

SECTION 5 — FIRE FIGHTING MEASURES

Explosion Risk: In case of concentrated airborne product keep at distance.

Flammable Class: Flammable at high temperatures, combustible, will help to sustain a fire.

General Hazard: evacuate personal downwind of fire to avoid inhalation of irritating and/or harmful fumes and smoke

Extinguishing Media: use over measure water spray or dry chemical powder

Hazard combustion products: carbon monoxide and carbon dioxide

Fire-fighting procedure: use water to wet down dust to prevent generation of dust clouds. Remove burned or wet wood dust to an open area after fire is extinguished.

Fire-fighting equipment: Respiratory and eye protection are required for fire-fighting personal. Full protective equipment (Bunker gear) and self-contained breathing apparatus should be used for all indoor fires and any significant outdoor fires.

Sensitive of static discharge: When pneumatically transported, static discharge may occur

SECTION 6 — ACCIDENTAL RELEASE MEASURES

If material is released in populated area it should be removed by sweeping or vacuuming as soon as possible. Torrefied material is a fuel and should preferable be disposed of means of burning.

- Remove all sources of ignition
- Wear appropriate personal protective equipment
- Avoid dust. Careful handling will reduce damage to the torrefied material and therefore the amount dust produced to the air
- Avoid oxidizing agents

SECTION 7 — HANDLING AND STORAGE

HANDLING

- Use appropriate personal protective equipment (as specified in Section 8)
- Handle in well-ventilated area
- Avoid breathing dust
- Avoid contact with eyes or skin
- Handle and use in a manner consistent with good industrial/manufacturing techniques and practices
- Wash thoroughly after handling

STORAGE

- Freshly torrefied material is oxidative for a period of time, depending on feedstock, degree of torrefaction and cooling time after reactor exit. Therefore storage should be under oxidation controlled atmosphere by dosed controlling oxygen intake during respective time.
- Store in a segregated and approved area. Access routes for fire-fighting must be free.
- Keep in a cool and ventilated area away from combustible materials.
- Avoid all possible sources of ignition (spark or flame).
- Use only appropriate electrical apparatus for use in the presence of combustible dust.

SECTION 8 — EXPOSURE CONTROL / PERSONAL PROTECTION

ENGINEERING CONTROLS

If user operations generate dust, make use of explosion proof equipment and ventilation equipment to assure airborne levels are below established exposure limits.

PERSONAL PROTECTIVE EQUIPMENT

Eyes Protection: Wear safety glasses or safety goggles.

Skin Protection: Where contact is likely wear protective gloves (nitrile rubber recommended).

Respiratory: Wear dusk mask (P2 filter) during handling.

Work Hygienic Practices: Clothing with long sleeves or an overall and protective skin cream or gloves increase personal hygiene on physical contact with the material.

SECTION 9 — PHYSICAL AND CHEMICAL PROPERTIES

Torrefied material exists in form of chips, powder with varying particle size and in pressed form to pellets or briquettes. For powder and briquettes data is not available yet.

Form:	Chips	Pellets
Particle Size: <i>Referring to ISO 17225-1*</i> *still under development	<i>ISO 17225-1 Table-5*</i> <i>Between 5 mm to 100 mm</i>	<i>ISO 17225-1 Table – 4*</i> <i>Length: 10 – 30 mm</i> <i>Diameter: 6 mm or 8 mm</i>
Color:	<i>dark brown to black grainy material</i>	
Odor:	<i>light scorch / charred wood smell</i>	
Product density (at 20°C):	<i>200 – 300 kg/m³</i>	<i>600 – 800 kg/m³</i>

Bulk density (at 20°C):	180 – 300 kg/m ³	600 – 800 kg/m ³
pH-Value:	<i>not applicable</i>	
Auto-Ignition Temperature - layer: (EN 50281-2-1:1999)	> 320°C	<i>Has to be evaluated</i>
Auto-Ignition Temperature - cloud: (EN 50281-2-1:1999)	> 490°C	<i>Has to be evaluated</i>
Lower Dust Explosion Limit: (EN 14034-3)	60 g/m ³	<i>Has to be evaluated</i>
Explosion pressure: (EN 14034-1:2004)		<i>Has to be evaluated</i>
Kmax: (EN 26184-1: 1993)	101 bar m/s	<i>Has to be evaluated</i>
Minimum Ignition Energy: (EN 13821:2003)	> 1000 mJ	<i>Has to be evaluated</i>
Water Solubility:	< 0,1% swell in water	<i>Has to be evaluated</i>
Viscosity:	<i>Not applicable</i>	
Melting Point / Boiling point:	<i>Not applicable</i>	

SECTION 10 — STABILITY AND REACTIVITY

Reactivity:

Over the time the product absorbs oxygen.

Stability:

Over time carbon monoxide or carbon dioxide or small amounts of methane are emitted

Conditions of Instability:

Higher temperature accelerate product decomposition

Moisture content accelerates product decomposition

SECTION 11 — TOXICOLOGICAL INFORMATION

Acute:

There is no toxicological information available for the material.

Carcinogenicity:

Product is not listed under IARC, NTP, OSHA as carcinogen hazardous material.

There is no information regarding carcinogenicity for the material.

SECTION 12 — ECOLOGICAL INFORMATION

Experimental ecological data are not available.

SECTION 13 — DISPOSAL CONSIDERATIONS**General:**

Refers to Section 6 Accidental Release Measures for additional information

Disposal Comment:

Dispose of waste at an appropriate waste disposal facility according to current applicable laws and regulations.

SECTION 14 — TRANSPORT INFORMATION

This material is yet not tested and / or classified under IMO dangerous goods. The product is combustible and sustains a fire. Torrefied biomass has been classified in ADR 4.2 and should be stored and transported according accessory prescribed rules.

UN-Number : 1361 [Carbon]

Symbols: Low oxygen risk area; No smoking; EX-area

CAS-Number: see section 1

EINECS-Number: *not available* (240-383-3 for charcoal)

RID/ADR Class: ADR 4.2

ADNR Class: not applicable

IMDG Class: not applicable

ICAO / IATA Class: not applicable

SECTION 15 — REGULATORY INFORMATION

EUROPEAN COMMUNITY EEC LABEL AND CLASSIFICATION

R(isk) Phrases:

R 36/37 Irritating to eyes and respiratory system

R 38 Irritating to skin

S(afety) Phrases

S 16 Keep away from ignition sources – do not smoke

S 22 Avoid breathing dust

S 24/25 Avoid contact with skin or eyes

S 26 In case of contact with eyes, rinse immediately with plenty of distilled or clean/drinking water and seek medical advice

National Legislation

A Chemical Safety Assessment according to EC 1907/2006 has not been done yet.

SECTION 16 — OTHER INFORMATION

Given information is based on our present knowledge but do not constitute a guarantee for any specific product features and do not establish a legally valid contractual relationship.

It is the user's responsibility to determine if this information is applicable. Notice that some of the information in this MSDS may not apply necessarily be applicable to products manufactured by other producers.

Authors are not responsible for any error or omissions, or for the results obtained from the use of this information and are not responsible for any direct, indirect, special, incidental, or consequential damage, or any other damages whatsoever and however caused, arising out of or in connection with the use of the information in this MSDS, or in reliance on that information, whether the action is in contract, tort (including negligence) or other tortious action.

Date: February 2013

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State of Issue: Preliminary

Abbreviations

ADNR: European Agreement regarding the international transport of hazardous goods by inland waterways.

CAS: Chemical Abstract Service registration number.

EEC: Dangerous Substances Directive 67/548/EEC

EINECS: European Inventory of Existing Commercial Substances.

IARC: International Agency for Research of Cancer (UN World Health Organization)

ICAO/IATA: International Civil Aviation Organization, International Air Transport Organization.

IMDG: International Maritime Code for Hazardous Goods mg/m³ Milligram per cubic meter.

IMO: International Maritime Organization (UN)

NTP: National Toxicology Program (U.S. Department of Health & Human Services)

OSHA: Occupational Safety and Health Administration (U.S. Department of Labor)

RID/ADR: European agreements for the stipulation of agreements regarding the international transport of hazardous goods by train (RID) and by road (ADR).

UN: substance identification number is a four digit number that identifies a hazardous substance during transport.

4 Outlook

Intense research about torrefied biomass is conducted within the 42-months SECTOR project. Due to the variation of several parameters, such as the type of biomass used, the process-parameters or possible treatment methods, final conclusions about a general chemical composition of the torrefied end products cannot be made presently. Therefore, the potential risks and hazards are not assessed and described finally at this stage.

In order to evaluate these risks, reliable and repeatable measurement techniques are necessary to assess the differences and quantities in the final products and by-products. Additionally, relevant practice tests are necessary, e. g. the product must be linked to the requirements of a power station. To evaluate such tests the development of aligned measurement methods to quantify the composition of the torrefaction products which is liberated during and after the process is a pre-condition.

Several physical and chemical properties required for the MSDS are not known yet and have to be evaluated in detail during the next years. Further it has to be clearly stated which form and particle size (powder, chips, pellets, briquettes) of the torrefied material this is relevant for. Especially the classification and parameters for flammability and the explosibility of dust are measures of high concern.

When it refers the chronic effects of health and safety aspects reference shall be given to European standards as well as to further North-American standards such as ACGHI, ASHREA and NIOSH.

Storage conditions are of particular importance, as this can result in further issues, and potential environmental hazards, such as the release of potentially toxic leachate and how firefighting measures have to and can be designed.

5 References and Material

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