Influence of minerals' nature and concentration on the gasification of cypress wood sawdust chars

Simona Bennici, Lionel Limousy, Khouloud Haddad, Mejdi Jeguirim

Université de Haute-alsace, CNRS, IS2M UMR7361, F-68100 Mulhouse, France

simona.bennici@uha.fr

BACKGROUND

o diminish greenhouse gas emission (CO_2)

Renewable: biomass energy is a renewable resource.

Dependency on fossil Fuels is reduced.

Carbon Neutral.

Widely Available.

Helps Reduce Waste.

Can be used in various forms. It can be used to produce methane gas, biodiesel and other biofuels.

It can also be used to directly generate heat or to generate electricity using a steam turbine.

It can produce **chars**, with a wide panel of applications.

Various source





WOOD WASTE VALORISATION PROCESSES

Energy context

- Reduction of fossil fuels
- Increasing energy demand
- Greenhouse gases (CO_2 emission)

Biomass: Renewable energy

Thermochemical conversion

- Combustion
- Pyrolysis
- **Gasification**

GASIFICATION

The gasification process involves three steps [1] :

- Drying
- Pyrolysis
- Gasification of char → **limiting step of the whole process[2]**

Study of the reactivity of the chars from lignocellulosic biomass to CO_2 and steam

Reactivity of the char is governed by several parameters:

-Temperature - Pressure - Heating rate	Pyrolysis parameter	→	- Chemical structure - Inorganic content - Porosity	**Char properties**

1 . *McKendry P. Energy production from biomass (Part 3): Bioresour Technol 2002*

2. *Dupont, C., Boissonnet, G., Seiler, J.-M., Gauthier, P., Schweich, D , Fuel 2007*

CHARS' REACTIVITY

Influence of the biomass char structure

- Correlation between the decrease in the gasification reactivity and the increase of the carbonaceous uniformity structure
- influence of inorganics (3-5)

The effect of the properties of lignocellulosic biomass chars on their reactivity under CO_2

T … la, Mg, Ca)

1. Biomass Preparation and Impregnation

2. Chars Production under Slow Pyrolysis conditions

3. Chars Properties Characterization

4. Gasification tests and Reactivity measurments under CO_2

3 . Nzihou A , Stanmore B, Sharrock P, A reviw of catalysts for the gasification of biomass char with some reference to coal , Energy , 2013

4. Z. Bouraoui, M. Jeguirim, C. Guizani, L. Limousy, C. Dupont, R. Gadiou, Thermogravimetric study on the influence of structural, textural and chemical properties of biomass chars on CO_2 gasification reactivity, Energy, 2015.

5. S. Bennici, M. Jeguirim, L. Limousy, K. Haddad, C. Vaulot, L. Michelin, L. Josien, A. Zorpas Influence of CO2 Concentration and Inorganic Species on the Gasification of Lignocellulosic Biomass Derived Chars, Waste Biomass Valor DOI 10.1007/s12649-019-00658-1, 2019.

SAMPLES PREPARATION

Biomass
eparation

- Raw material : Cypress Sawdust
- Grinding using mechanical crusher
- Sieving in different fractions
- Drying : 60°C, 24 h
- Selected fraction : Dp < 400 µm

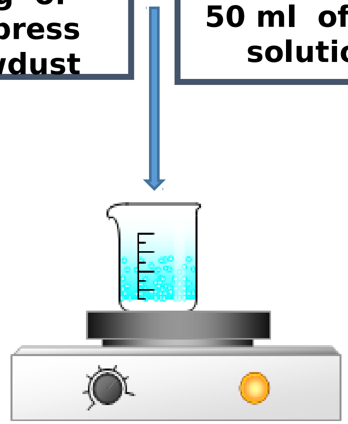
Impregnation Solutions

- KCl : 5-25 g/l
- NaCl : 10-20 g/l
- $MgCl_2$: 10-50-100 g/l
- $CaCl_2$: 10-50-100 g/l

Cypress Sawdust Impregnation

5 g of Cypress Sawdust

50 ml of salt solution



Mixture stirred (400 tr/min) at room temperature

Washing Procedure

Only for the washed chars _

CHARS PRODUCTION

Char Production Conditions:

- Sample mass: 5 g
- Temperature range : 10 K/min
- Flow rate (Argon) : 25 NL/h
- Temperature : 800°C
- Residence time at the maximal temperature: 1h

Textural Properties

Sample id	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)	BET Surface area (m^2/g)
Wash-Char	0.231	0.204	499.9
Raw-Char	0.195	0.149	481.8
K-Char	0.192	0.181	410.2
Na-Char	0.193	0.182	466.2
Mg-Char	0.210	0.191	495.2

Pyrolysis yields

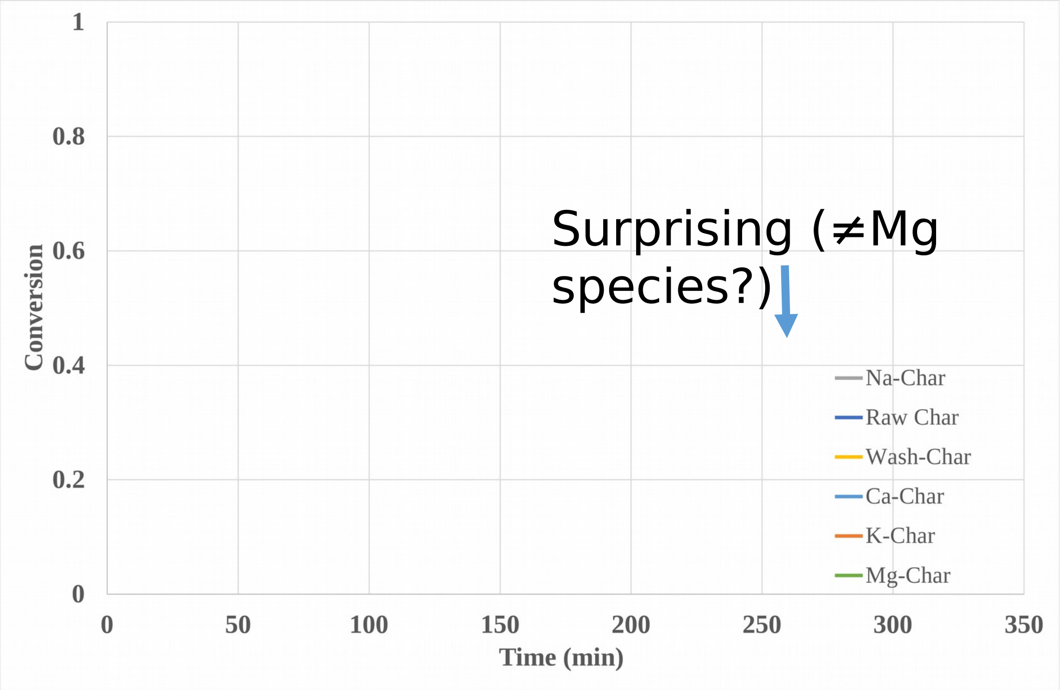
RS-char	26.54
WS-char	24.18
K-char	27.63
Na-char	27.13
Mg-char	24.05
Ca-char	24.60

Char yield increases in the presence of potassium and sodium due to the condensation of light VOCs

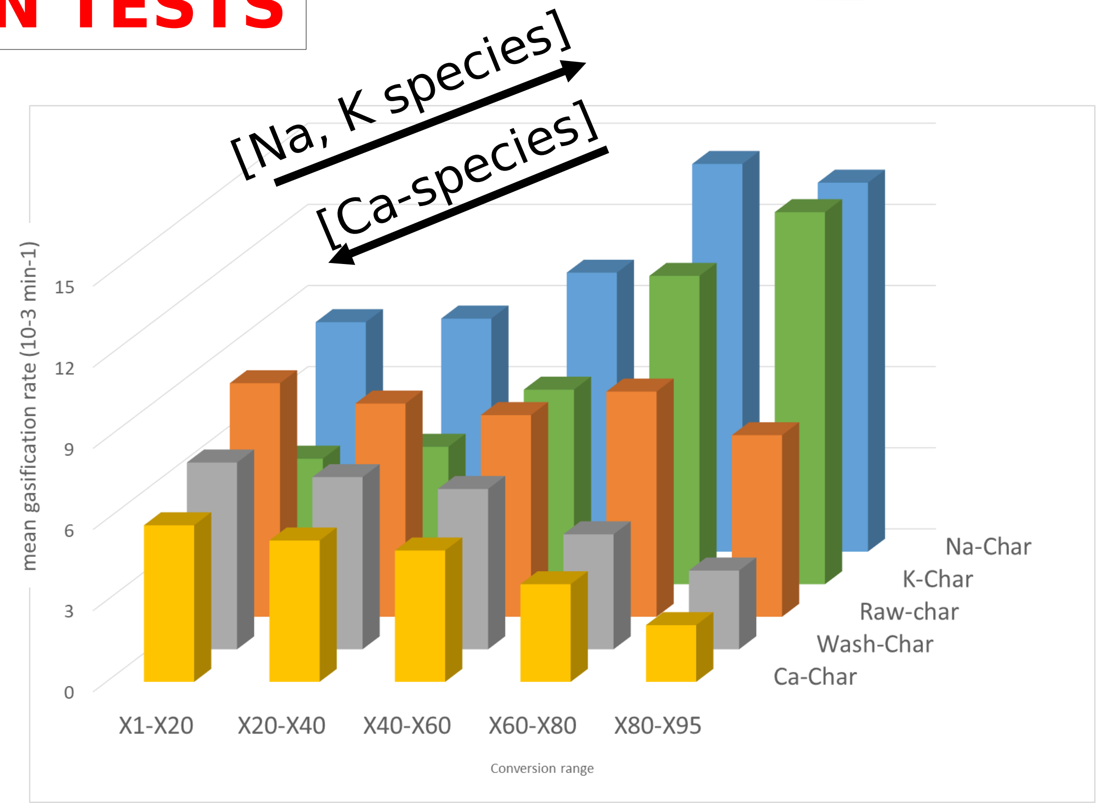
Mineral Contents

	Raw -char	Wash -char	K-Char	Na-Char	Mg-Char	Ca-Char
K (mg/g)	1.60	0.48	5.70	0.05	0	0.12
Na (mg/g)	0.95	0.23	0.34	7.95	0	0.33
Mg(mg/g)	0.89	0.73	0.15	0.16	6.60	0
Ca (mg/g)	3.02	3.55	2.43	2.86	1.84	5.01

GASIFICATION TESTS



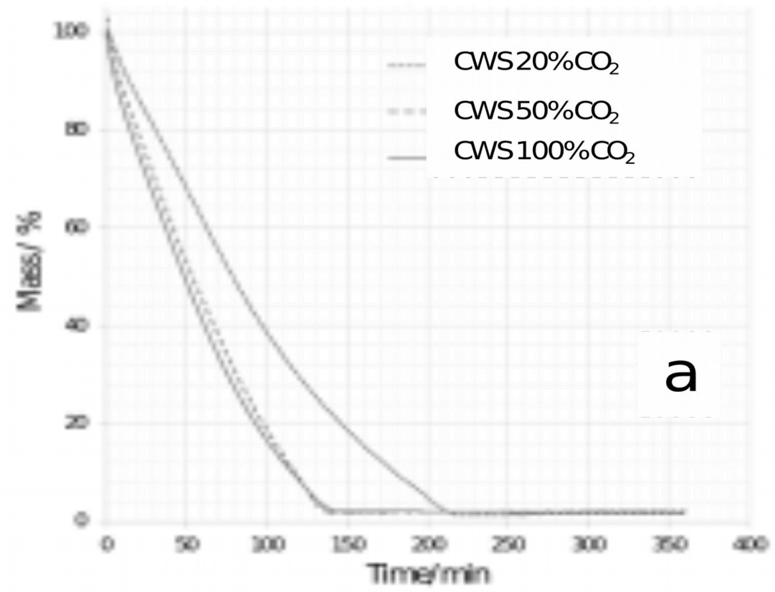
Conversion versus time during the CO_2 char gasification



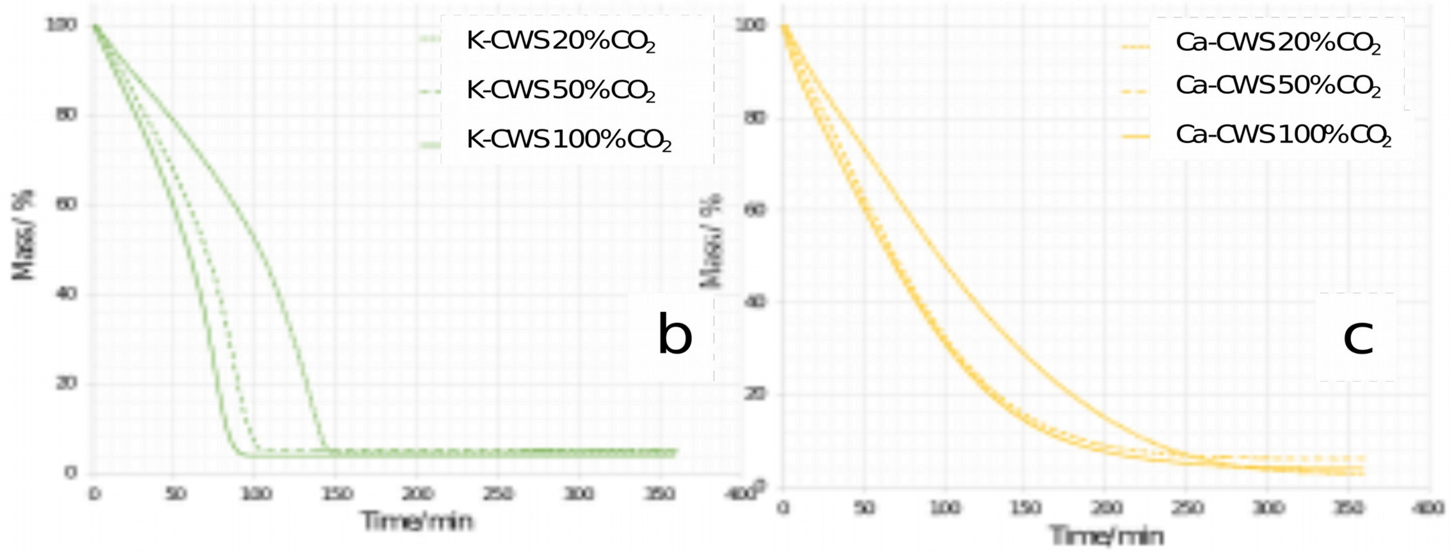
Gasification rate versus conversion ratio of the different chars

	Raw-Char	Wash-Char	Na-Char	K-Char	Ca-Char	Mg-Char
$\tau_G(min)$	128	209	100	143	293	*
$\bar{v}_g(10^{-3}\,min^{-1})$	7.74	4.91	10.4	6.88	3.93	1.43*

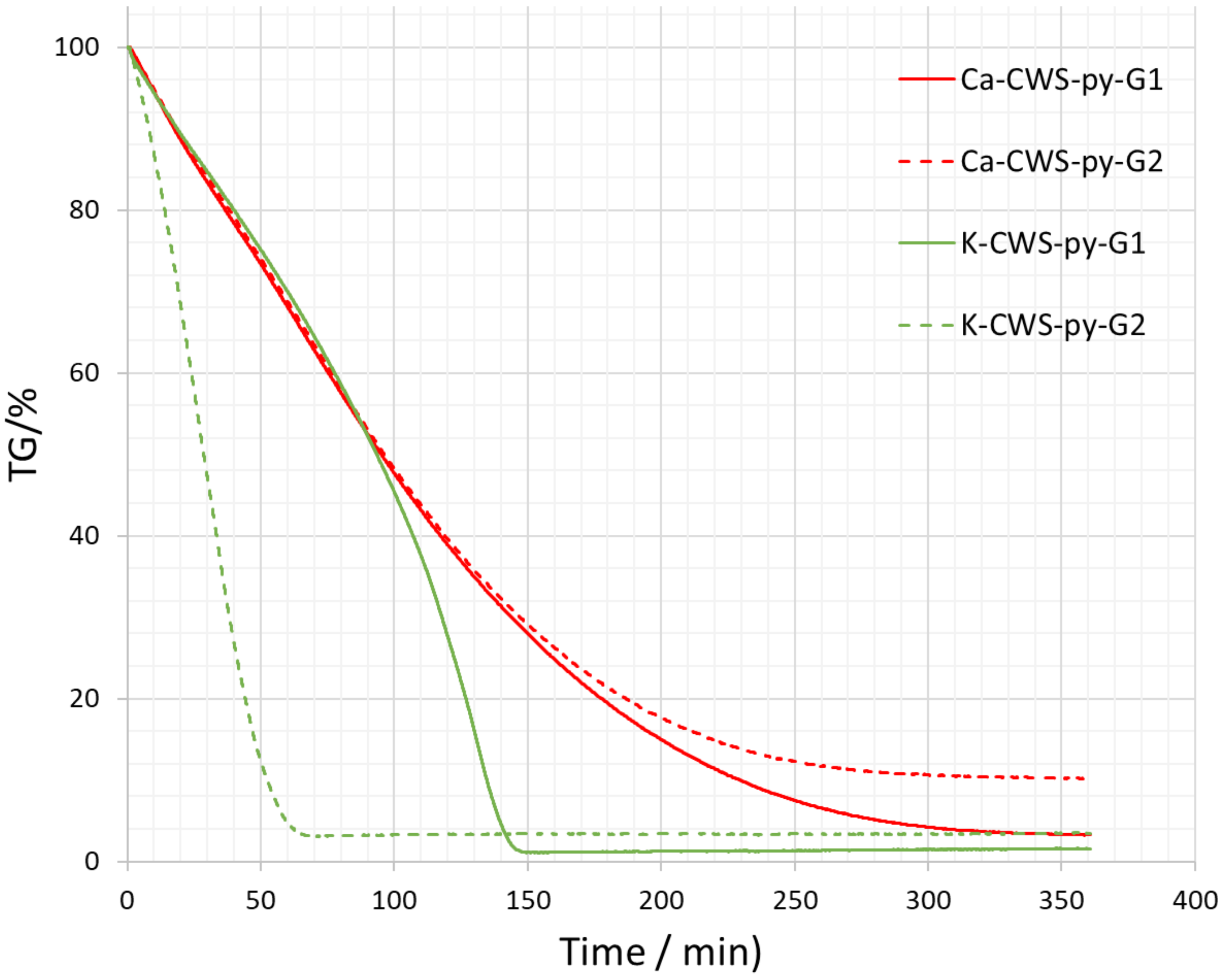
GASIFICATION



The slope of the curves increases with the concentration of CO_2 in the gasification stream



GASIFICATION: ASHES CONCENTRATION



Successive gasification experiments: the second is carried on in presence of the ashes (residue) of the first gasification

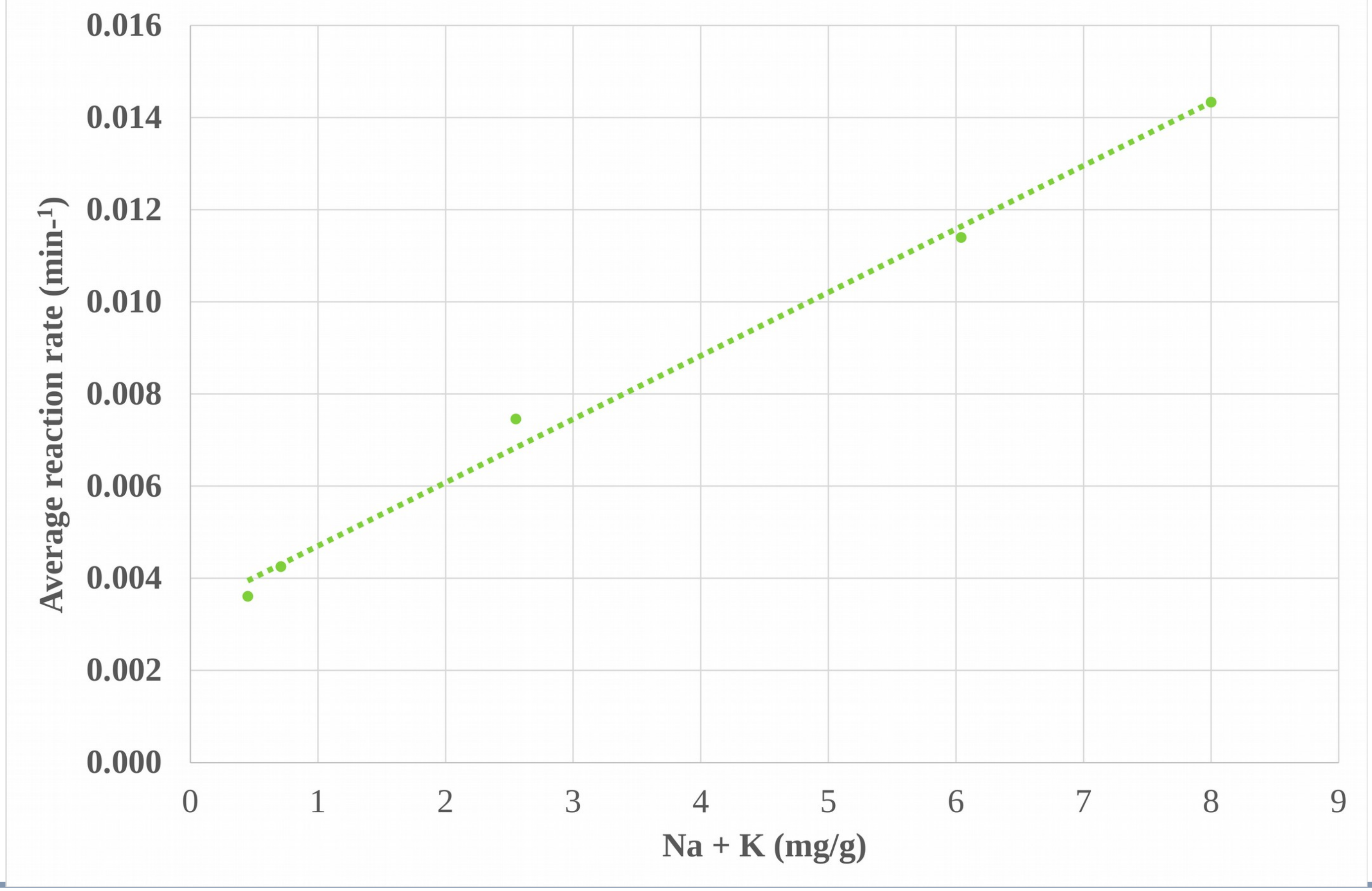
The K-species catalytic effect is enhanced by the increasing in ashes concentration

No enhancement of the Ca-species inhibitor effect is detected with the presence of Ca-rich ashes

Need to identify the active species

CORRELATION CHAR PROPERTIES / REACTIVITY

Comparison of the average reaction rate at high conversion with K+ Na content



➔ A correlation between the average reaction rate at high conversion and K+Na Content

CONCLUSIONS

The gasification rate values for Mg-char, Ca-char and washed char (that contains Ca as principal inorganic element) slightly decrease with the conversion during gasification, demonstrating the **inhibiting effect of calcium and magnesium species.**

Differently, the **catalytic effect operated by K and Na-species** is strongly enhanced by concentrating them into the char. At around 50% conversion the gasification rate take-off, demonstrating the catalytic effect of K and Na-species, **regardless of other parameters as the modified porosity, and morphology.**

Clearly identified for the present samples, these types of catalytic and inhibiting effects need to be deeply analysed in order to discern between the **direct impact of inorganics** to those related to **morphological changes** (i.e. development of micro and ultramicroporosity), and to the formation of **new surface functionalities**.

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materials

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Guest Editors:

Dr. Mejdi Jeguirim
Institut de Sciences des Matériaux de Mulhouse, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France

mejdi.jeguirim@uha.fr

Dr. Simona Bennici
Institut de Science des Matériaux de Mulhouse, IS2M - CNRS UMR 7361 - UHA, 3 rue Alfred Werner, 68093, Mulhouse Cedex, France

Simona.bennici@uha.fr

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Message from the Guest Editors

Dear colleagues,

There is an overwhelming compulsion in the development of new materials aiming to diminish the environmental footprint of processes in the energy field and to adapt their properties to target applications. A different approach is to create new and target materials for a definite application by varying the synthesis and activation conditions and methodology during preparation. This way, numerous new materials have recently been developed for specific applications in the field of energy. Thanks to the advances in material science, several energy storage and production processes have been transformed/reconverted into clean processes (biofuel industry, fatal energy recovery, renewable energy storage, etc.).

The topic of this Special Issue is the implementation of new materials in clean processes in the energy field:

- Biosourced material for energy recovery (biofuel, chars, etc.);
- Materials and composites for energy storage (PCM, salt hydrate, zeolites, etc.);
- Materials and catalytic materials for energy related processes (biofuels production and purification, biogas purification, etc.).

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Special Issue

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- Materials and catalytic materials for energy related processes (biofuels production and purification, biogas purification, etc.).

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.... THANK YOU !!!