NO-WASTE

1.4.2013-31.3.2017

Utilization of Industrial by-products in Environmental Protection

NEWSLETTER 8

No Waste –project boosting the circular economy world-wide

No-Waste aims at boosting the circular economy and have an impact on the clean environment. Since the start of the No-Waste in April 2013, the members of the project consortium have worked towards reaching the goals of the project. The six work packages of the project, mentioned below, have dealt with valorization of different types of waste, production of clean fuels, improvement of HTC processing, development of the new waste-based adsorbents, fertilizers and catalytic materials and production of chemicals from waste gases. The results are published in several national and international conferences and journals. Dissemination of the results will continue also after the end of the project.

Catalysis and adsorption technologies have been in the central role in the research*.* The novel catalytic materials have been developed for the clean fuel production and utilization of the waste gases. Also very efficient carbon-based materials have been developed for the water purification purposes. The collaboration between the countries in the materials development has been fruitful and fluent. The materials originating from one country have travelled to another country for processing or characterization purposes and very often to third partner for testing purposes. The researchers participating the project have benefitted from the materials, infrastructure and knowhow available in the partnering countries. This has allowed the work go further than possible within only one country, and improved the efficiency of the research work. More information on the research results can be found later in this Newsletter.

The project results have attracted the attention of the local media. The researchers seconded via No-Waste have presented the project, their work and the results in the newspapers, radio and TV. Especially Brazilian and Moroccan radio and TV have been interested in the No-Waste. Within the framework of No-Waste one international conference was organized in El Jadida Morocco in 2016. The conference had about 100 participants from different countres. More details about the conference can be found later in this newsletter.

The general aim of the No-Waste was the creation of a long-term cooperation network related to sustainable production and waste material utilization. This aim was achieved via the transfer of the researchers and know-how between the research groups participating the No-Waste. In numbers, we mobilized in total 60 persons between the European and Non-European countries. In total, 188 exchange months were realized. The collaboration within the framework of No-Waste resulted in several new national and international research project applications and new projects, that include also collaboration with the industry and new research partners outside No-Waste consortium. In the future we aim at continuing the collaboration and the work aiming at more sustainable future with less waste and healthier environment!

Contacts:
e-mail Riitta Keiski riitta.keiski@oulu.fi
e-mail Satu Ojala satu.ojala@oulu.fi
e-mail Niina Koivikko niina.koivikko@oulu.fi

WP 1 Hydrogen and synthesis gas production from waste
University of Poitiers

WP 2 Valorisation of wastes from olive and argan production
University of Chouaib Doukkali

WP 3 Production of valuable chemicals from CO_2 and organic gases
University of Oulu

WP 4 R&D on the HTC technology to valorize industrial by-products and wastes,
Federal University of Applied Sciences, Goiania

WP 5 Utilisation of methane originating from coal mining
Dalian Institute of Chemical Physics

WP 6 Research on the HTC process: Product design
Trier University of Applied Science

May 2017
Newsletter by Coordinator

Environmental pollution is a global problem. Unsustainable production of goods, improper treatment of waste, emissions to air and water, and inadequate legislation cause growing problems to human beings and the nature. The urgent need for reducing environmental load coming from industry, agriculture and communities demands for novel ways of thinking. NO-WASTE collaboration will attack to this current problem by developing environmentally sound and sustainable utilization and valorization methods for wastes and emissions. **The aim is to create valuable new products and renewable energy vectors to minimize the amount of waste as well as emissions to air and water.** The frame of operation of NO-WASTE allows a great number of green chemistry related possibilities to create networks of knowledge between the scientists of different fields (science, engineering, economy, health) in different countries.

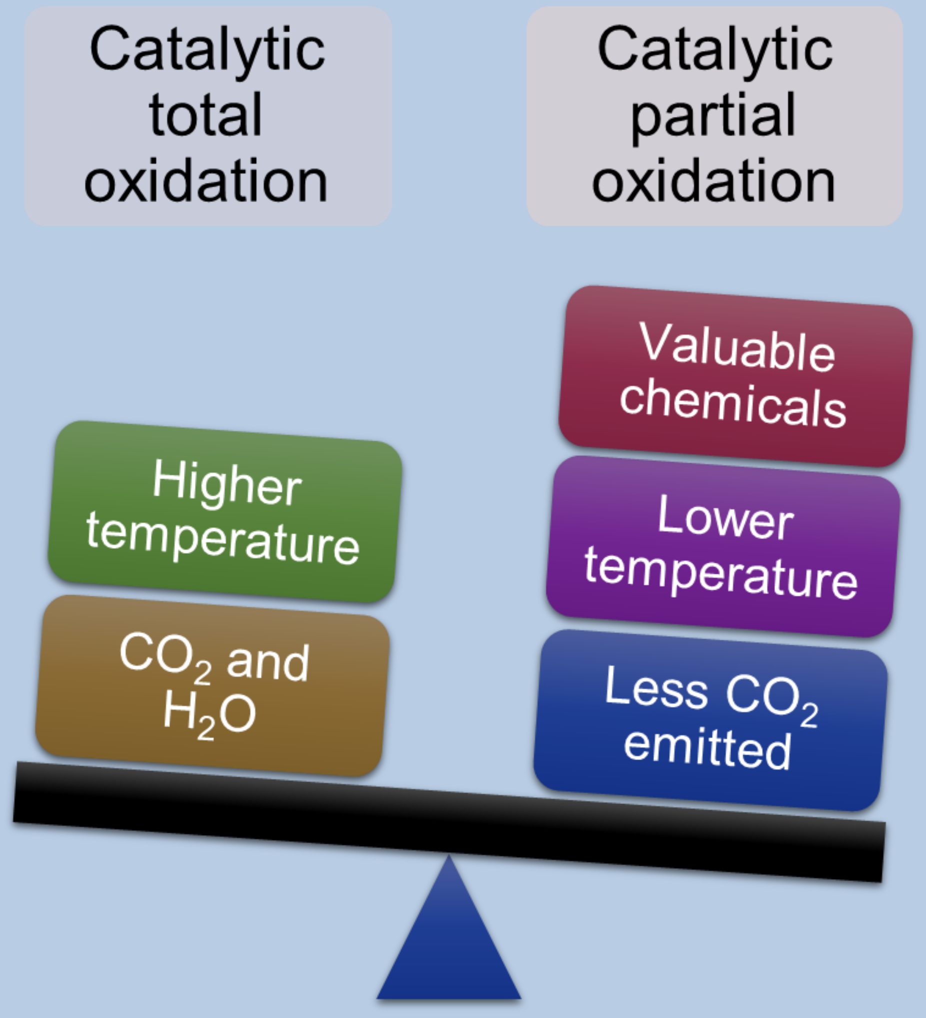
NO-WASTE

1.4.2013-31.3.2017

Utilization of Industrial by-products in Environmental Protection

NEWSLETTER 8

Utilization of Volatile Organic Compounds



Utilization and recycling of waste and old consumer products, such as journals, clothes and bewerage bottles is quite familiar concept for the most of the people. However, the utilization of waste gas is a less common issue.

During the past years, the mitigation of CO_2 has been a shared topic of discussion among the researchers and the legislative people. In fact, the CO_2 emissions are considered as the major contributors to the Global warming. In addition to CO_2, the emissions of volatile organic compounds (VOC) are giving their contribution to the greenhouse effect. As such, their global warming potential is multifold compared to the CO_2, and when they are treated, they are very often oxidized to CO_2 and water as well as other final oxidation products.

VOCs offer several novel possibilities for the utilization. To minimize the effect of the VOC to the environment and human health, more interesting approach would be the utilization of VOC. There are several different possibilities for the VOC utilization that could be derived e.g. from production processes of different organic chemicals. During the No-Waste, we published one quite comprehensive review article in "Catalysis" -journal on the utilization of VOC by using the catalytic approaches. There we estimated that the largest potential for VOC utilization based on the information on the emitted compounds in different sectors would be found in the utilization of aromatic compounds, alkanes and alkenes. [1]

Currently the most typical way in the utilization of VOC is its use in the power generation. According to our considerations, currently the most interesting action line with faster response to the market, would be the utilization of VOC in the synthesis gas (H_2 + CO) and hydrogen production. Furthermore, certain types of VOC could be used in high-value chemicals production as well.

More research is needed in catalyst development. Independent of the application, the catalyst development is in the core of this research. During the recent years, in the research group of Environmental and Chemical Engineering at the University of Oulu, Finland, the VOC utilization research has focused on the Pulp Mill emission utilization, which is a relevant traditional sector of industry in Finland. The emission stream originating from a pulp mill contains significantly high amount of methanol among the reduced sulphur-compounds (TRS). From this mixture, methanol and methyl mercaptan could be used in the formaldehyde production, but the rather high sulfur-content causes problems with the catalysts currently used in the processes of formaldehyde production from methanol. During the No-Waste we have found several potential catalysts that could be used in the proposed process, and that, at the same time, seem to be more resistant towards sulfur. Sientific journal publications will appear on these results in near-future.

Are the VOCs an economical source of H_2? During the No-Waste, we have also started the research efforts aiming at VOC utilization in hydrogen production. While this research is under way, we expect having the publishable results quite rapidly due to the existing information and the significant efforts made in the World towards clean fuel production. Wouldn't it be great to drive your hydrogen-driven car that fuel has been produced from the emissions of the industrial facilities nearby the town you are living? This would be a great way to apply the concept of the distributed energy production and at the same time contribute of the clean air of your own town!

The work in WP3 was done in collaboration with UP, UCD and UP.

References

[1] Ojala, S. et al. Utilization of Volatile Organic Compounds as an Alternative for Destructive Abatement, Catalysts, 2015, 5, 1092-1151. (Open access)

Contacts:

e-mail Satu Ojala satu.ojala@oulu.fi

e-mail Niina Koivikko niina.koivikko@oulu.fi

Production of H_2 via reforming

Today, dihydrogen produced in the world is obtained from the fossil hydrocarbons (natural gas or naphtha), mainly by reaction with water (steam reforming), oxygen (partial oxidation), or by combination of these two reactants, i.e. by oxidative steam reforming. These processes lead to the unavoidable formation of carbon dioxide (a greenhouse gas) as the main by-product.

Figure 1. Photo of the members of the PhD thesis jury of Dr. Asmaa Drif at University Chouaïb Doukkali in El Jadida, Morocco (16th February 2016).

Another way for H_2 generation involves the utilization of CO_2 as reactant in the so-called dry reforming reaction for producing synthesis gas, since a molar H_2/CO ratio around 1 may be obtained. This synthesis gas can be used as the feedstock to chemical synthesis, like methanol, or in liquid fuel production *via* the well-established Fischer-Tropsch reaction.

Methane dry reforming (Eq. 1) was studied earlier in 1928 [1] by Fischer and Tropsch, but it has attracted much attention during the last two decades, since it is now considered as a greenhouse gas consuming reaction [2-5]. Moreover, methane and carbon dioxide can be directly produced from raw materials such as agricultural waste *via* the biogas generation process. Another interesting way, that is more recently studied [6-8], consists of using ethanol obtained from 2nd generation biomass (wheat straw, corn stover, bagasse) instead of methane for the dry reforming reaction. It is the so-called reaction of Dry Reforming of Ethanol (Eq. 2).

$$CH_4 + CO_2 \leftrightarrow 2\,CO + 2\,H_2 \quad \text{(Eq. 1)}$$
$$\Delta H^0_{298} = +246.9 \text{ kJ mol}^{-1}$$

$$C_2H_5OH + CO_2 \leftrightarrow 3\,CO + 3\,H_2 \quad \text{(Eq. 2)}$$
$$\Delta H^0_{298} = +297.1 \text{ kJ mol}^{-1}$$

The possibility to produce ethanol from biomass, leads ethanol to be a very attractive renewable source for hydrogen production. The dry reforming of bioethanol or biogas may be thus regarded as a CO_2-depleting reaction for two reasons:

- CO_2 is first consumed as a reactant and
- the CO_2 which might be emitted by the combustion of the final Fischer-Tropsch product is compensated by the CO_2 consumption occurring during the growth of the crops at the origin of the bioethanol or biogas production**.**

All these reactions involved are highly endo-thermic and require the utilization of a catalyst to reach significant hydrogen or synthesis gas yields. The main challenge of WP1 “Hydrogen and synthesis gas production from waste” was to optimize the catalytic systems for these two reactions. In cooperation between University of Poitiers, University Chouaïb Doukkali and University of Oulu, a supported noble metal catalyst was developed by modifying alumina support by various M_xO_y oxides (M = Zr, Mg, Ni, Ce, La). The highest performances, obtained for Rh/NiO-Al_2O_3, in both methane and ethanol dry reforming reactions were explained by the presence of the $NiAl_2O_4$ spinel phase, avoiding the deactivation of rhodium that could occur by migration in alumina, and the high dispersion of Rh favoured by the presence of nickel particles at the support surface. This work was part of the PhD thesis of Dr. Asmaa Drif (Figure 1). The results of the research have also been published in

Drif, A., *et al.* ***Applied Catalysis A: General***, 504 (2015) 576-584.

Contact:
e-mail Nicolas Bion nicolas.bion@univ-poitiers.fr

Efficient catalysts via sololution combustion and by using an inexpensive clay material

In supported noble metal catalysts, only the surface atoms of the noble metal particles are useful for the catalytic reaction. For cost efficiency a high dispersion of the metallic particles is thus required to improve the surface/volume ratio of noble metal atoms. However, even in very small 4-6 nm metal particles, only small fraction of the total noble metal atoms are utilized for reactant conversion.

The complete dispersion of noble metals can be obtained when noble metal is added as ions within an oxide support. In WP1, University of Poitiers, University Chouaïb Doukkali and Dalian Institute of Chemical Physics reproduced the common work on the concept of noble metal ionic catalyst developed by Hegde *et al.* [10]. In this concept the solution combustion method is proposed to solve the dispersion problem.

Figure 1. $Ce_{1-x}Pd_xO_{2-\delta}$ catalyst preparation according to Hegde et al. (a) Aqueous solution of ceric ammonium nitrate, Pd nitrate, and oxalyldihydrazide, (b) the solution burning with a flame, and (c) the oxide product. Reprinted with permission from [10]. Copyright (2017) American Chemical Society.

This method, described in Figure 1 for $Ce_{1-x}Pd_xO_{2-\delta}$ catalyst, was applied in No-Waste-project to the preparation of ceria-zirconia-supported rhodium catalyst, which enabled to reach the synthesis gas yield, expected at the thermodynamic equilibrium at 750°C, in the reaction of dry reforming of methane and ethanol. The composition of the catalyst exhibiting the best performances was $Rh_{0.01}Ce_{0.49}Zr_{0.5}O_2$ corresponding to 0.7 wt% Rh.

The method of impregnation was also undertaken for comparison and a similar catalytic activity was observed for Rh 1 wt-% impregnated on $Ce_{0.5}Zr_{0.5}O_2$ prepared by solution combustion method. It is worth noting that the latter catalyst contains 30% more noble metal for the same performance.

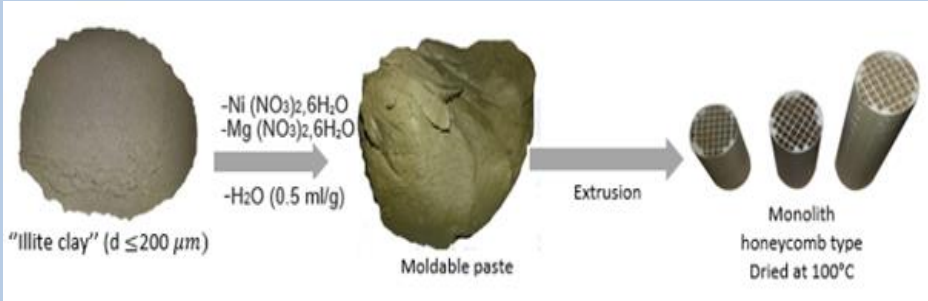


Figure 2. the different steps of the preparation of honeycomb monolith-shaped illite clay.

Finally, in the last study, in which University of Poitiers collaborated with Dalian Institute of Chemical Physics with the association of University Abdelmalek Essâadi in Morocco (not included in No-Waste consortium), the autothermal reforming investigations have been carried out with Ni-containing honeycomb monolithic catalyst.

The monolithic catalysts were prepared using an illite clay to which nickel phase and basic promoters such as magnesium were added into moldable mixture paste before extrusion as described in the Figure 2. This approach avoids washcoating of the monolith and reduces significantly the preparation steps and additional costs due to the use of easily available resources, such as natural clay. The catalyst formulations promoted with 3 wt% of magnesium presented better performances than the same catalyst without Mg. Magnesium was supposed to favor the formation of NiO-MgO solid solution leading to partial reduction of NiO that lower agglomeration of the nickel particles.

This work shows a promising potential for application of the clay honeycomb monolith as a catalyst for biogas reforming. It could help further development of low cost innovative catalytic materials offering the possibility to give higher economical added value to local resources and contribute to local sustainable development.

References

[1] F. Fischer, H. Tropsch, *Brennstoff. Chem.* 3 (1928) 39-46.
[2] A.M. Gadalla, B. Bower, *Chem. Eng. Sci.* 43 (1988) 3049-3062.
[3] J.R. Rostrup-Nielsen, J-H. Bak Hansen, *J. Catal.* 144 (1993) 38-79.
[4] S.C. Tsang, J.B. Claridge, M.L.H. Green, *Catal. Today* 23 (1995) 3-15.
[5] M.C.J. Bradford, M.A. Vannice, Catal. *Rev.-Sci. Eng.*, 41 (1999) 1-42.
[6] K. de Oliviera-Vigier, N. Abatzoglou, R. Gitzhofer, Can. J. Chem. Eng. 83 (2005) 433-468.
[7] J.D.A. Bellido, E.Y. Tanabe, E.M. Assaf, *Appl. Catal. B*, 90 (2009) 485-488.
[8] A.M. da Silva, K.R. de Souza, G. Jacobs, U.M. Graham, B.H. Davis, L.V. Mattos, F.B. Noronha, *Appl. Catal. B.* 102 (2011) 94-109.
[9] A.W. Budiman, S-H. Song, T-S. Chang, C-H. Shin, M-J. Choi, *Catal. Surb. Asia* 16 (2012) 183-197.
[10] M. S. Hegde, G. Madras, K. C. Patil, *Acc. Chem. Res.*, 42 (2009) 704-712.

Main scientific production on dry reforming reaction generated with No-Waste project

- Drif, A., *et al.* ***Applied Catalysis A: General***, 504 (2015) 576-584.
- Drif, A., *PhD* of University Chouaïb Doukkali, February 2016.
- Drif A., *et al.* "**CO_2 reforming of ethanol on supported Rh catalysts**", poster presentation in TOCAT7, 1-6 june 2014, Kyoto, Japan.
- Drif A., *et al.* "**Reformage à sec de l'éthanol sur des catalyseurs à base de Rh**", poster presentation in GECAT national meeting, 12-15 May 2014, Cluny, France.

Contact:
e-mail Nicolas Bion nicolas.bion@univ-poitiers.fr

HTC-treatment of Sewage Sludge

Wastewater sludge is a problem. Sludge from wastewater treatment is produced world-wide. It poses a range of problems, that are often not solved.

- Waste water sludge contains often heavy metals and hazardous microorganisms
- When not properly treated and use in landfills it takes up precious space of the existing landfills. Additionally, such disposal produces greenhouse gases and it is a risk for the ground water. Therefore, such disposal is not considered as a sustainable.
- The agricultural use can cause the concentration of heavy metals in food materials
- Nutrients are wasted if sewage sludge is treated in waste incineration and cement producing plants

As part of the No-Waste project the University of Applied Sciences Trier focused on the treatment of sewage sludge by hydrothermal carbonization. During the recent years a wide range of research has been performed concerning the treatment of sewage sludge. The focus of the research was in the production of materials, that can be safely used in agriculture and give advantages concerning the improvement of agricultural soils.

This gives several advantages:

- Untreated sewage sludge has a high water content (around 75% mass) and is difficult to dewater. After the HTC-treatment, the dewatering properties are much improved.
- During and after the HTC-process nutrients like phosphorus can in principle be recovered.
- The heavy metals can be partially transferred to the liquid phase, from where a separation is possible
- The HTC-coal has properties that are similar to other biochars and contains a high level of nutrients.

Sludge can be transformed to a fertilizer. An important part of the No-Waste activities was a joint German-Brazilian project, where we focused on biochar from hydrothermally treated sewage sludge as a soil conditioner for small farmers in the Brazilian federal state of Goiás.

This work was co-funded by the Friedrich-Ebert-Stiftung, Germany and it was carried out in cooperation with the Universidade Federal de Goiás, Prof. Dr. Wilson Mozena Leandro, the Bergische Universität of Wuppertal, Prof. Dr. Jörg Rinklebe and the Helmholtz Centre for Environmental Research (UFZ), Dr. Elke Schulz. During this project, chemical and physical analyses were performed with sewage sludge from Brazil and Germany to produce a high quality sewchar via hydrothermal carbonization of sewage sludge and use the sewchar as a fertilizer for plants typically grown by small farmers in Brazil. Germination tests were carried out with salad, rice, beans and radish. Using sewchar as fertilizer different results were observed depending on the crop plant and the sewchar concentration. **In absolute terms sewchar had better effect as fertilizer for the cultivation of rice and 0.5% sewchar concentration had the highest rice dried biomass.**

The toxicity of sewchar to the fauna of soil and water was assessed via ecotoxicological tests, using different concentrations of sewchar. The first article in relation to this research has been submitted to the Journal of Environmental Geochemistry and Health under the title: "Effect of biosolid hydrochar on toxicity to earthworms and brine shrimp".

The effect of sewchar additions on plant growth and soil properties was also assessed and compared with mineral fertilizer, using bean as a crop plant.

The Ph.D student Tatiane Melo together with members of the local settled rural families association, discussing the requirements for the use of sewchar as potential fertilizer.

Another important part of the work was to study the acceptability by small farms of using this sewchar as potential fertilizer. For this purpose several meetings took place with settled rural families in the area of Palmeiras de Goiás, Brazil.

Contacts:
e-mail: Ulrich Bröckel
u.broeckel@umwelt-campus.de
e-mail Michael Bottlinger
m.bottlinger@umwelt-campus.de

NO-WASTE

1.4.2013-31.3.2017

Utilization of Industrial by-products in Environmental Protection

NEWSLETTER 8

International symposium Environment 2016: Eco-Processes, remediation and/or recovery of waste and effluents for a sustainable environment

The opening of the symposium

One of the biggest dissemination highlights of the No-Waste was realized in February 2016 in El Jadida-Morocco; where Chouaïb Doukkali University, the Faculty of Sciences and the Department of Chemistry of El Jadida-Morocco organized an international symposium "Environment 2016: Eco-Processes, remediation and/or recovery of waste and effluents for a sustainable environment". The symposium was organized by the group of Professor Rachid Brahmi composed of 13 PhD students and 6 professor researchers and it was held between 17.-19.2.2016. After two months, on the road of COP21 in Paris.

This symposium, organized under the project of No-Waste, gathered several national and international professors and researchers (France, Germany, Tunisia, Finland, Brazil, China, Morocco, Algeria) who were invited to present their latest technical and scientific results in the field of preservation and protection of the environment. This scientific event was also an opportunity for young PhD students to present their research results and discuss about them with specialists in the field. During the symposium 10 Keynote lectures were held, 39 oral presentations and 41 poster presentations, of which abstracts were compiled in the conference proceedings book.

Organization committee

This event was a good meeting point for the No-Waste partners and to create contacts outside the current concortium. Moroccan national TV was following the event and several researchers were interviewed by the TV improving the visibility of the environmental research for the Moroccan public.

This intensive, highly focused three-day symposium brought together many brilliant professors and researchers in the field, such as, Prof. Charles Kappenstein and Prof. Catherine Batiot-Dupeyrault from Poitiers University in France, Prof. Jean-François Lamonier from University of Lille in France, Prof. Tarik Chafik from University Abdelmalek Essaadi in Tangier and Prof. Tapio Salmi from Åbo Academy University, Turku, Finland, as well as many other professors, researchers and doctoral students.

The primary objective of the symposium was the creation of a long-term cooperation related to the sustainable production and waste material utilization as well as to offer a good opportunity for networking for the participants. The more specific goal was to share the knowhow in highly interactive environment and provide the attendees the recent and practical environmental research results related to applications which have a contribution to the reduction of solid, liquid and gaseous waste of several polluting industries, agriculture and communities by transferring the waste to valuable products. Moreover, in order to encourage the young researchers to develop their research work and to support their participation in the conference, there were prizes for the best oral presentation and poster presentation. The winners of the best oral presentation were Mahmoud El Ouardi, Barhoum Kharbouch and Souakaina Rida. The best poster presentations were prepared by Aziz Boutouil, Houyem Hafdi and Asmae El Hassouni.

The No-Waste –project and the related research reached very important visibility during this event and due to the positive impact and new interests risen, similar events may be continued after the end of No-Waste.

The winners for the best oral and poster presentation

Group picture of the participants

Contacts:
e-mail: rachid.brahmi@univ-poitiers.fr

NO-WASTE

1.4.2013-31.3.2017

Utilization of Industrial by-products in Environmental Protection

NEWSLETTER 8

HTC Products – Solution for industrial residues

Fig. 2 - Bagasse storage

Hydrothermal carbonization (HTC) is a thermochemical conversion process that transforms biomass into solid products with high surface area, such as a graphene structure, and some thermal stable materials. The HTC process involves spontaneous restructuration of the organic materials through dehydration and polymerization, and it generates carbon particles with polar functional groups. The experimental conditions include temperature ranges from 180°C to 250°C, and the internal pressure of 16 to 45 bar of an autoclave containing a suspension of biomass with water mixed with catalysts. Depending on the reaction conditions, different biochars with distinguishingly specific physical-chemical properties are produced.

The state of Goiás is located in the Central West of Brazil, and became a strategic region for food and energy (sugarcane) crops production, and pharmaceutical industries. The sugarcane process for bioethanol (and sugar) production generates bioelectricity in using bagasse (straw), and applies as biofertilizers the residues of filter cake and vinasse (effluent). Wastes from other industry segments are normally disposed in open waste dumps, landfills. Incineration process is rare and limited by high costs. In the case of the sugarcane industries in Goiás, there were, between 2015 and 2016, 73 million tons of sugarcane harvested and the related generated residues of 20.4 million tons of "bagasse", which are burned inefficiently for energy production [Ref.: UNICA – Union of Producers of Sugarcane, 2016].

The No-Waste Brazilian Group has applied HTC process to transform bagasse and other organic wastes into biochar and other structured materials as well. The obtained products from residues are environmentally interesting, such as the activated carbon or catalytic supporter (Fig. 4), and biofertilizers or soil conditioners.

Fig. 3 - Biomass residue from sugarcane process

In this work, the life cycle exhausted ionic exchange resins were tested in HTC to synthetize polymeric activated carbon (PAC). The PAC products showed surface carboxyl, phenolic and lactonic functional groups. These groups favour metal anchoring sites, indicating characteristics of catalyst support materials.

The HTC offers the possibility to produce carbon particles in the nanometre range. The use of certain residual polymers contributes to the synthesis of nanostructured materials.

Possible applications are, for example, to prepare adsorbents, nanoparticle materials (catalysts), nanowires, or indeed to be used as energy storage. The hydrochar as HTC product from biomass (filter cake) can be applied to soil amendments since the HTC-hydrochars cation exchange capacity (CEC) values increased up to 346.5 mmolc kg^{-1}, compared to raw filter cake (CEC) of 229.5 mmolc kg^{-1}.

Fig. 1 - Sugarcane ***Saccharum (37 species)***

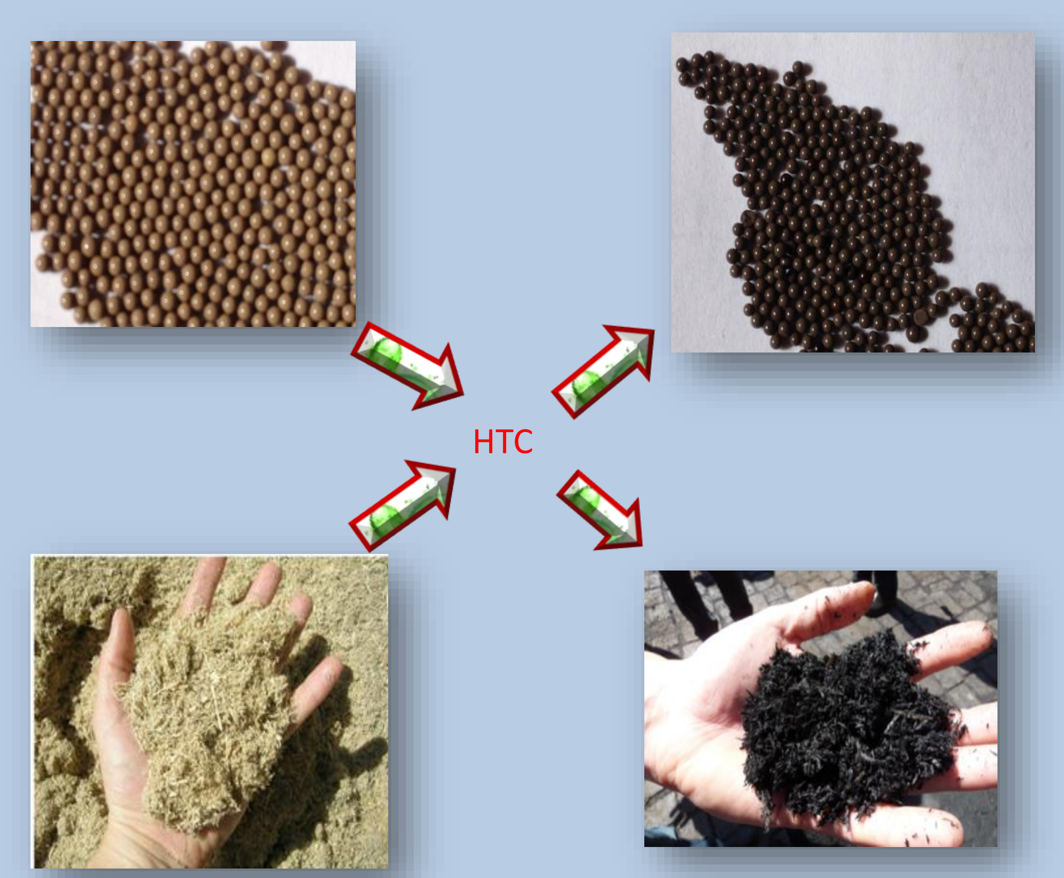


Fig. 4 - Hydrochar from ionic exchange resins waste and sugarcane bagasse

The water holding capacity (WHC) of the same material reached values from 234.7 to 334.8% m/m.

Regarding the Brazilian normative instruction IN SDA n° 35/2006 of the MAPA (Ministry of Agriculture), the HTC-hydrochars show higher values than the minimum recommended CEC of 200.0 mmolc kg^{-1} and WHC 60% for soil conditioners or amendments. **The use of biochar (the carbonaceous HTC materials) to soil amendments impacts positively the characteristics of water and nutrient release of the soil and consequently the positive effects on vegetation growth.** The long-term stability of the HTC biochar in the soils, and its applications contribute to the global carbon budget of carbon sequestration. A soil benefit is expected with applications of 0.5 tons up to a maximum of 100 tons per hectare. The positive conclusions in using HTC biochar as soil conditioner or soil improvement are as follows:

- Storage and nutrients release control for plants;
- pH soil regulator;
- Drop of nutrient lixiviation to groundwater;
- Enhancement of the soil water storage capacity;
- Sequestration of greenhouse gas emissions (N_2O, CH_4);
- Improvement of living microbiological fauna;
- Carbon sequestration; and
- Potassium (K) ion was mobilized significantly in replacing water by vinasse in the HTC process, and the K-availability grew by about 250% compared to the non-treated ashes.
- The Brazilian sugar cane industry pointed to more than 34.000 kg of potassium per year (vinasse), which could be added to the HTC process additionally providing ashes enriched with soil K-nutrient.

Contacts:

e-mail Sergio de Oliveira
Dr_botelho@yahoo.com.br
e-mail Joachim Zang dr.zang@icloud.com
e-mail Warde Zang
warde@quimica-industrial.com

NO-WASTE

1.4.2013-31.3.2017

Utilization of Industrial by-products in Environmental Protection

NEWSLETTER 8

Efficient solutions to utilize and mitigate the organic gases via catalytic combustion

Catalytic combustion is a process that oxidizes compounds using catalyst, and it has been proven to be a suitable alternative to conventional flame combustion for heat and power production. A stable combustion can be achieved at relatively low operating temperature. Almost no thermal NOx is formed, and only ultra-low levels of carbon monoxide and hydrocarbons can be observed. Nowadays, catalytic combustion is widely used for a variety of purposes such as emission control, gas cleaning, gas turbines, etc.

The combustion catalyst and the catalytic combustion technologies were developed in WP5, in Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Pellet form and monolithic catalysts were investigated, and their mass and heat transfer as well as reactions were studied, as described in Fig.1.

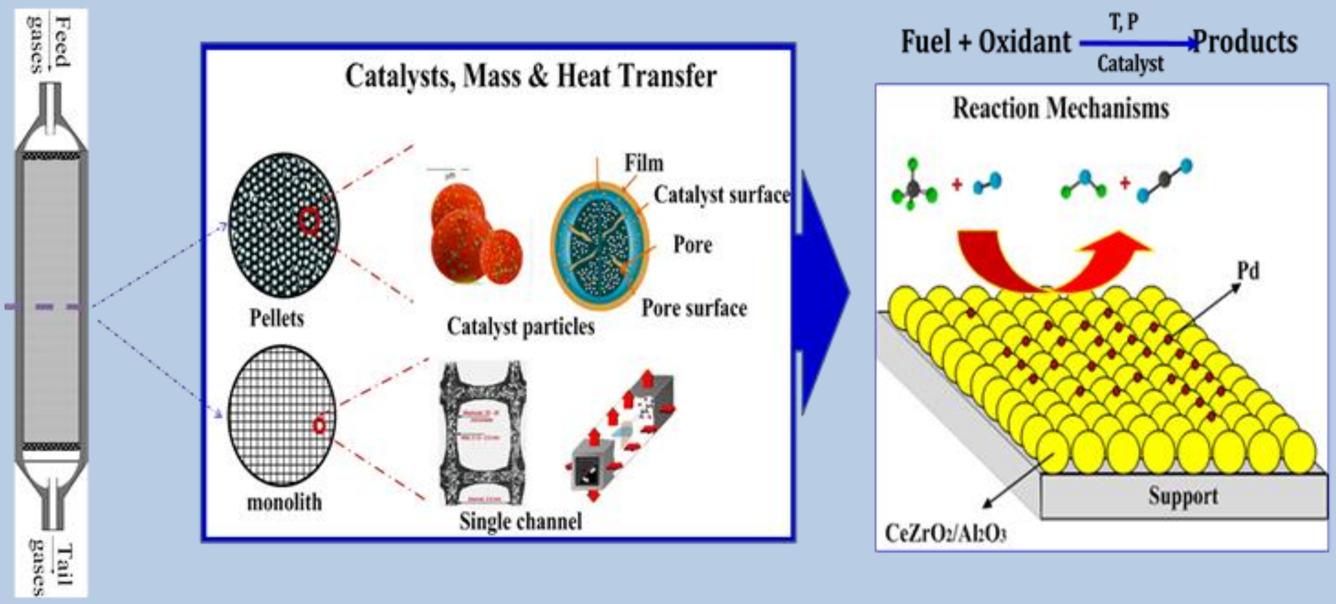


Fig.1. Technical principle of catalytic combustion (Reactor, catalysts, mass and heat transfer)

During the research, a controllable synthesis of catalytic materials was developed. A series of catalysts were designed to satisfy the requirements of special applications, such as Noble metal catalysts (Pd, Pt, Ru), metal oxide catalysts (Co_3O_4, Mn_2O_3 etc) and pervoskite as well as hexaaluminate catalysts. For metal oxide catalysts, Co_3O_4 with different morphologies were synthesized controllably, and noble metal (Pd) was supported on them. The catalytic combustion performance of these catalysts were evaluated in CO/CH_4 catalytic combustion. The catalytic activities of flower-like Co_3O_4 and hexagonal plate-like Co_3O_4 were comparable to those of noble metal catalysts due to the preferred exposure of more active {111} crystal plane. In case of cubical Co_3O_4 the {001} plane is the dominantly exposed crystal plane [1].

When Pd was supported on Co_3O_4 with different morphologies, similar observation was made. The catalytic performances of Co_3O_4 and Pd/Co_3O_4 are strongly dependent on the surface O_{ads}/O_{lat} in CH_4 and CO oxidation [2].

Futhermore, a facile scheme was proposed to promote $LaMnO_3$ perovskite catalyst for the combustion of methane. This catalyst is able to tolerate the temperatures up to 700^{o}C [3].

Meanwhile, to meet the requirements of diverse coal mine methane concentrations, the process diagrams were designed. Based on the design, pilot systems were integrated and run. A recycle process was developed to control the adiabatic temperature rise. A 300Nm^3/h unit (Fig.3) was designed to remove catalytically the oxygen in coal mine methane (CMM). Thus, the potential safety hazard can be thoroughly eliminated owing to the occurrence of oxygen, when the CMM was purified.

For ventilation air methane (VAM), it is difficult to sustain autothermal operation of the process due to low methane concentration (0.2 vol.% - 0.75vol.%). Thus, the catalytic reverse flow reactor or the regenerative catalytic reactor (RCO) was designed and integrated, as shown in Fig.4. The transient and steady state behaviours of the reactor were experimentally investigated [4].

Based on the relevant studies, catalysts and process, the commercial process design package (PDP) was compiled.

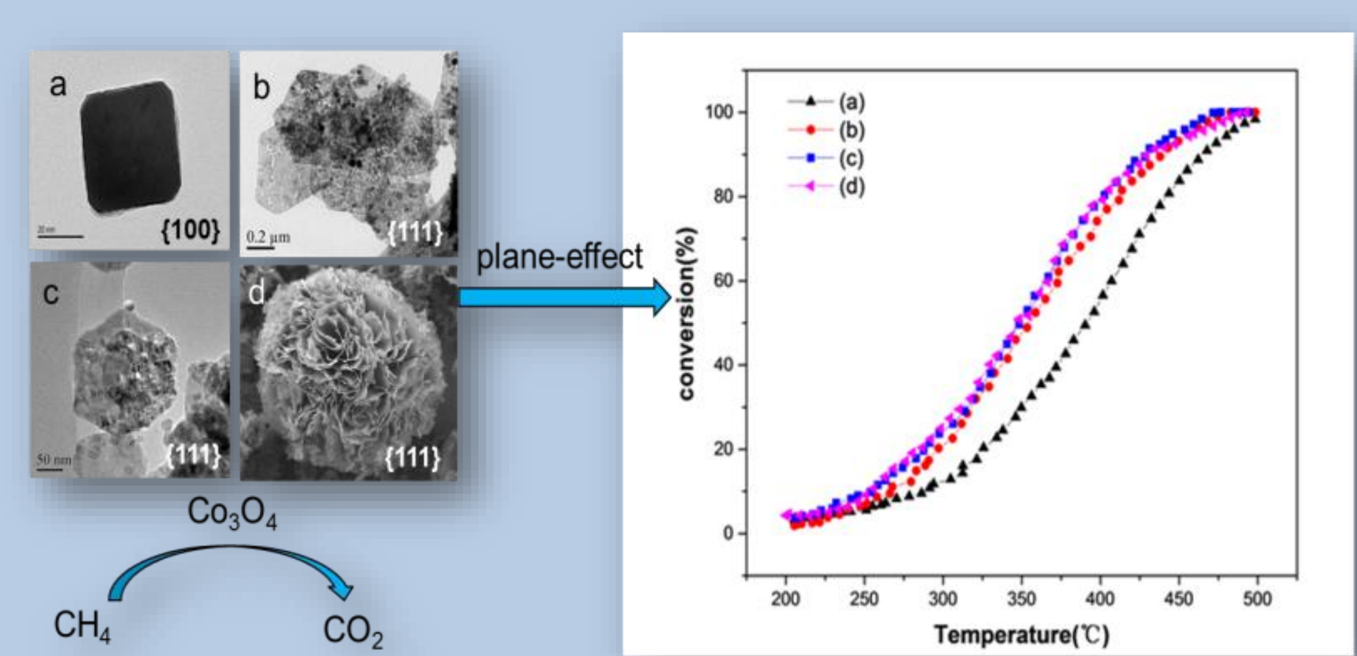


Fig.2. The morphology-dependence of Co_3O_4 for methane combustion

Fig.3. A 300Nm³/h unit for the catalytic deoxidation in CMM

As the important pollutants, volatile organic gases (VOCs) are given considerable attention in China. Recently, we focus on the R&D of the catalysts to treat the VOCs, which contain sulfur and chlorine, or bromine. Certain bench-scale systems in that connection were tested in the industrial field.

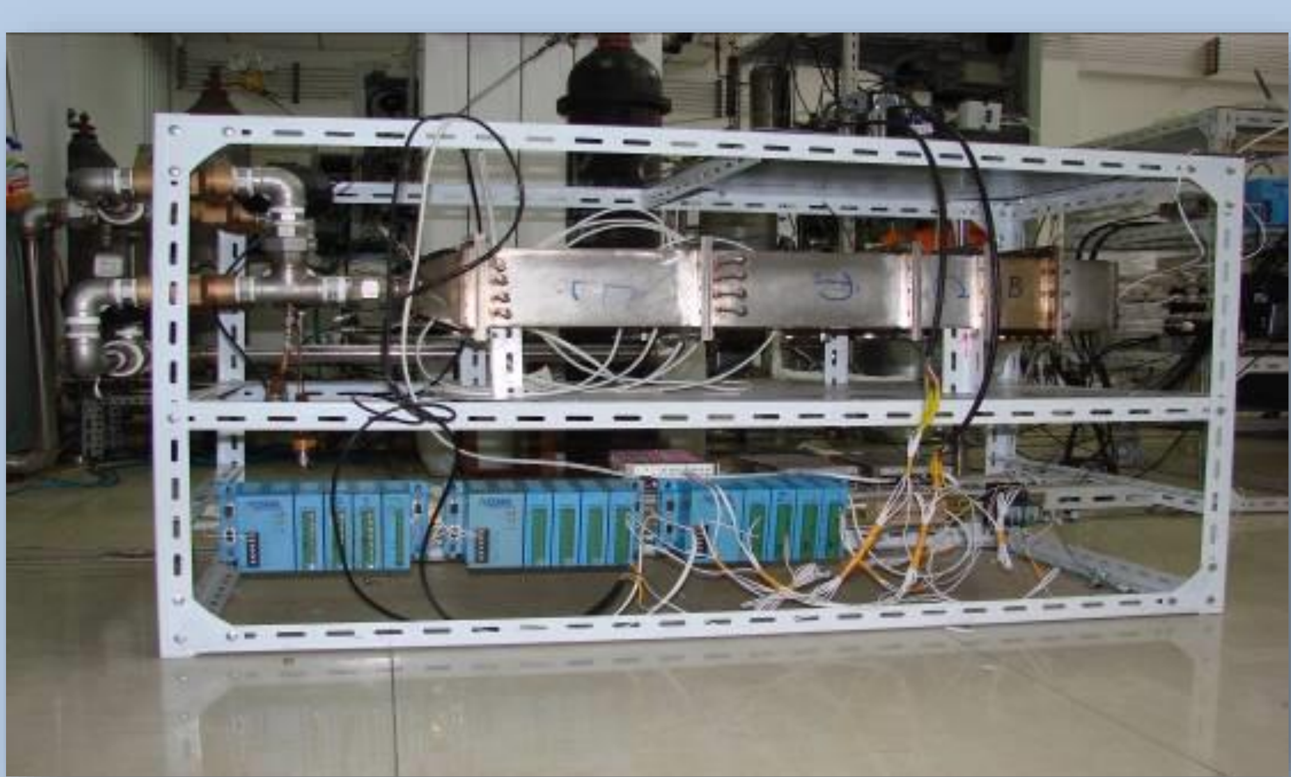


Fig.4. A 40Nm³/h RCO unit for the catalytic removal of methane in VAM

References

[1]Z.P.Chen, S. Wang, Applied Catalysis A: General, 2016, 525: 94-102.

.[2]Z.P.Chen, S. Wang, Applied Catalysis A: General, 2017, 532: 95-104.

[3]Y. Ding, S. Wang, Catalysis Communications, 2017，97(5): 88-92.

[4]S. Wang, S. Wang, Industrial & Engineering Chemistry Research, 2014, 53: 12644 -12654.

Contact:

e-mail Wang Sheng wangsheng@dicp.ac.cn

e-mail Wang Shudong wangsd@dicp.ac.cn