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Production of small batches finalized

SUCCESS - Industrial steam generation with 100% carbon capture and insignificant efficiency penalty - scale-up of oxygen carrier for chemical-looping combustion using Environmentally sustainable materials	*Keywords:* *Spray drying, Oxygen carrier*
Work package: 1 – Confirmation of industrially available raw materials for spray-dried materials	
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Objective

In the previous FP7 INNOCUOUS project, a spray-dried calcium-manganese-based material of general composition $CaMn_{1-x-y}Mg_xTi_yO_{3-\delta}$ was found to have excellent properties as oxygen carrier for natural gas combustion. The key objective of work-package 1 is to confirm adequate properties of this material when production of this material uses commercial raw materials, i.e. materials available in quantities sufficient for large-scale production and at a suitable price. It was decided to focus on obtaining viable manganese oxide and titanium oxide powders, as these are deemed to be the most expensive and difficult materials to obtain at the scales which will be employed in the SUCCESS project. Several types of Mn-materials and titanium oxides have been tested for the production of $CaMn_{1-x-y}Mg_xTi_yO_{3-\delta}$ oxygen carriers by spray drying. This deliverable provides an overview of all the produced small batches.

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Introduction

In the INNOCUOUS project, two spray-dried calcium-manganese-based oxygen carriers (C14, C28), of general composition $CaMn_{1-x-y}Mg_xTi_yO_{3-\delta}$, were selected as viable alternatives to baseline Ni-based oxygen carriers. The oxygen carriers showed stable and high reactivity in both the Chalmers 10kW and Vienna 120kW CLC units. This material was manufactured by a rather pure Mn oxide and TiO_2. Since these types of oxides are rather expensive, with unknown availability, it would be better to change these materials to commercial raw Mn and Ti oxides in order to reduce the price for the oxygen carrier production. In addition, these commercial materials must be available in sufficient quantities for the scaling up of the chemical looping concept. Furthermore, the calcium-manganese-based material produced by this raw Mn oxide and Ti oxide should still show good oxygen carrier performance. Therefore, different commercial raw Mn oxides and Ti oxides are tested for the production of small batches of $CaMn_{1-x-y}Mg_xTi_yO_{3-\delta}$ oxygen carriers by spray drying.

Production of small batches

1. Production method

Based on previous experiments, it seems that the presence of Ti stabilizes the perovskite structure, which is beneficial for an oxygen carrier. Therefore, it was decided to focus on the production of oxygen carriers based on the C28 composition. Similar to the previous project, the Mn-based oxygen carriers were manufactured using the industrial spray-drying method. This method allows producing oxygen carrier particles with good free-flowing properties, high sphericity and homogeneity on the micro-scale.

To produce each small batch, a commercial Mn oxide or ore and Ti oxide, together with $Ca(OH)_2$, and MgO, were weighed and dispersed in deionized water with the necessary organic additives. Then, this suspension was homogenized by an horizontal attrition mill (Netzsch, Germany) prior to spray-drying. During spray-drying, the water based suspension was continuously stirred with a propeller blade mixer while being pumped to the 2-fluid spray-dry nozzle, positioned in the lower cone part of the spray-drier (type 6.3-SD, Niro, Denmark). The suspension is atomized into a large number of small droplets in the chamber of the spray-drier, which is filled with hot air from the top, thus creating a mixed flow regime. As such, the droplets quickly achieve a spherical shape due to surface tension effects. In addition, the large surface-to-volume ratio of the droplets allows rapid water evaporation resulting in dry particles, which are separated from the hot air. After spray-drying, the fraction within the required particle size range (150-300 µm) was separated from the rest of the spray-dried product by sieving. Finally, to obtain oxygen carrier particles with sufficient mechanical strength and with the desired crystalline phases, sintering was performed in air using a high temperature furnace (Entech, Sweden).

2. Overview of produced batches

An overview of all the spray dried small batches based on a commercial Mn oxide or ore is given in Table 1 and the batches based on a commercial Ti oxide are summarized in Table 2. All the materials in Table 1 are produced with a titanium oxide of Alfa Aesar, while all the materials in Table 2 are based on the Mn oxide Trimanox of Chemalloy. The batches based on a combination of a commercial Mn oxide/ore and Ti oxide are presented in Table 3.

Besides all the C28 batches, one batch based on the C14 composition was also spray dried for the Mn-ore Mangalox. This ore contains a lot of iron and iron may have the same stabilization effect as Ti. The acquired Mn-ore of Tshipi, the Sintec oxide of Eramet-Comilog and two ores of Eramet were not tested, because their particle size was too large to be processed for spray drying.

Table 1: An overview of all the spray dried small batches of calcium-manganese-based oxygen carriers based on a commercial Mn oxide or ore.

Compo-sition	Batch	Mn oxide	Thermal treatment	Amount of material	Sent to Chalmers on
C14	Sib001	Mangalox K45, Sibelco	4h @ 1275°C	50 g	16/12/2013
			4h @ 1300°C	50 g	
			4h @ 1325°C	50 g	
			6h @ 1335°C	50 g	3/03/2014
C28	Bas001	MnO, BassTech	4h @ 1350°C	100 g	27/01/2014
			4h @ 1375°C	100 g	
	Elk001	Micromax S, Elkem	4h @ 1350°C	100 g	
			4h @ 1375°C	100 g	
	Elk002	Colormax S, Elkem	4h @ 1350°C	100 g	
			4h @ 1375°C	100 g	
	Elk003	Colormax P, Elkem	4h @ 1350°C	100 g	
			4h @ 1375°C	100 g	
			4h @ 1350°C	700 g	14/04/2014
	Aut001	N60, Autlan	4h @ 1350°C	100 g	3/03/2014
			4h @ 1375°C	100 g	
	Aut002	N65, Autlan	4h @ 1350°C	100 g	
			4h @ 1375°C	100 g	
	CDMA001	CDMA, Erachem-Comilog	4h @ 1350°C	100 g	
			4h @ 1375°C	100 g	
			4h @ 1350°C	630 g	7/05/2014
	Sve001	XH1455, MB-Sveda AB	4h @ 1350°C	100 g	3/03/2014
			4h @ 1375°C	100 g	
	Era001	XH1452, Erachem-Comilog	4h @ 1350°C	100 g	
			4h @ 1375°C	100 g	
	xxxxxx	MnO_2-X, (NDA)	4h @ 1325°C	100 g	29/04/2014
			4h @ 1350°C	100 g	
	Era003	Hausmannite LM type, Erachem-Comilog	4h @ 1325°C	100 g	
			4h @ 1350°C	100 g	
	Sib002	Mangalox K45, Sibelco	4h @ 1325°C	100 g	
			4h @ 1350°C	100 g	

Table 2: An overview of all the spray dried small batches of calcium-manganese-based oxygen carriers based on a commercial Ti oxide.

Composition	Batch	TiO_2	Thermal treatment	Amount of material	Sent to Chalmers on
C28	Kro001	Kronos 2900, Kronos	4h @ 1350°C	100 g	30/04/2014
	Sac001	Sachtleben TR, Sachtleben	4h @ 1350°C	100 g	
	Cri001	AT-1, Cristal	4h @ 1350°C	100 g	
	Sac002	Sachtleben TP Hombikat M211, Sachtleben	4h @ 1350°C	100 g	

Table 3: An overview of all the spray dried small batches of calcium-manganese-based oxygen carriers based on a commercial Mn oxide/ore and Ti oxide.

Composition	Batch	Mn oxide	TiO_2	Thermal treatment	Amount of material
C28	Elk/Sac 001	Colormax P, Elkem	Sachtleben TP Hombikat M211, Sachtleben	4h @ 1325°C	100 g
				4h @ 1335°C	100 g
				4h @ 1350°C	100 g
				8h @ 1335°C	700 g
				8h @ 1335°C	700 g
	Elk/Kro 001	Colormax P, Elkem	Kronos 2900, Kronos	4h @ 1325°C	60 g
				4h @ 1350°C	60 g
	Elk/Sac 002 (other stoichiometry)	Colormax P, Elkem	Sachtleben TP Hombikat M211, Sachtleben	4h @ 1335°C	100 g
	Elk/Sac 003 (other stoichiometry)	Colormax P, Elkem	Sachtleben TP Hombikat M211, Sachtleben	4h @ 1335°C	100 g
	Elk/Sac 004	Colormax P, Elkem	Sachtleben TR, Sachtleben	8h @ 1335°C	800 g
				8h @ 1335°C	700 g
	Era/Sac 001	Hausmannite LM type, Erachem-Comilog	Sachtleben TR, Sachtleben	8h @ 1335°C	800 g
	Era/Sac 002	Hausmannite LM type, Erachem-Comilog	Sachtleben TP Hombikat M211, Sachtleben	8h @ 1335°C	800 g

Conclusions

Twelve different Mn oxides/ores and four different Ti oxides from various international suppliers have been used to produce small batches of $CaMn_{1-x-y}Mg_xTi_yO_{3-\delta}$ oxygen carriers by spray drying. One batch based on the C14 composition was manufactured with a commercial Mn-ore of Sibelco, which was sintered at four different temperatures (1275-1300-1325-1335 °C). Besides the C14 batch, twelve batches based on the C28 composition were spray dried with the available Mn oxides and ores. The first nine batches were sintered at 1350 °C and 1375 °C, while the last three were sintered at 1325 °C and 1350 °C. All these batches were produced with the rather expensive TiO_2 which was previously used in the Innocuous project. In addition, four batches were spray dried with commercial (cheap) TiO_2 from three different suppliers and sintered at 1350 °C. The Mn oxide in these last four batches was Trimanox of Chemalloy, which was also previously used in the INNOCUOUS project.

From the most promising Mn and Ti oxides, 5 different combined batches were spray dried and sintered between 1325 °C and 1350 °C. Of one combination, namely Colormax P and Sachtleben TP, two additional batches were spray dried with another stoichiometry than the current C28 composition.

Of each batch, about 1-2 kg of green material is produced by spray drying and 100 g of sintered product is obtained at each sintering temperature for the first characterisation tests at Chalmers. Furthermore, larger batches of about 600-800 g were sintered for tests in a 300 W reactor in order to make a material decision for upscaling.