Fuel Processing Technology 167 (2017) 511–523

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Selection of dolomite bed material for pressurized biomass gasification in BFB

Chunguang Zhou*, Christer Rosén, Klas Engvall

KTH Royal Institute of Technology, Department of Chemical Engineering and Technology, SE-10044 Stockholm, Sweden

A R T I C L E I N F O

Keywords:
Dolomite
Pores
Crystal
Pressurized fluidized bed
Gasification

A B S T R A C T

Dolomite is considered advantageous as bed material in fluidized bed gasification processes, due to its catalytic tar cracking and anti-sintering properties. However, in case of pressurized fluidized bed gasifiers, the use of dolomite is challenging. High temperature in the presence of steam favors the production of clean syngas due to the intensified cracking of tar in the presence of CaO, whereas it simultaneously increases the tendency of fragmentation of dolomite particles after full calcination. The present study was carried out to examine the influence of the properties of dolomite on the stability of dolomite in a pressurized fluidized bed gasifier, with the aim of determining criteria for dolomite selection. Glanshammar dolomite exhibited a better stability in the mechanical strength after calcination, compared to Sala dolomite. The corresponding change of micro-structure that occurred during dolomite chemical transformation was presented. The crystal pattern and Si distribution in the crystal lattice are the possible explanations for the superior performance of the Glanshammar dolomite compared to the Sala dolomite.

1. Introduction

Pressurized fluidized bed gasification is considered as an attractive solution to achieve an economical, as well as an overall efficient conversion system for biomass-based large-scale production of transportation fuels and chemicals [1]. Since the rate of gasification increases significantly in pressurized conditions [2], the size of pressurized gasifier can be reduced, compare to an atmospheric reactor with the same processing capacity. Pressurized fluidized bed gasification systems also have an advantage in integrated systems if gas streams with high pressure are needed in the downstream systems, such as Fischer-Tropsch Synthesis, integrated gasification combined cycle (IGCC), etc. [3] Nevertheless, there are a few challenges to address before industrial operation of a plant for production of transportation fuels and chemicals, such as ash sintering and bed agglomeration, as well as tar formation. A feasible method to reduce the risks of agglomeration is to use mineral based bed materials. Mg- or Ca-based bed materials, including magnesite and dolomite, are proposed for use in fluidized bed gasifiers utilizing biomass as fuel feedstock [4–6]. Dolomite has previously shown a good ability to decrease the risks of agglomeration in pressurized fluidized bed gasifiers [7]. Moreover, it is also regarded as an attractive material for catalytic tar cracking, which has been extensively investigated [8–14].

However, dolomites are soft, and may be susceptible towards attrition in the fluidized bed. The ability to sustain attrition in the bed depends on the materials structural properties [15,16] and the process conditions. To be able to select a proper dolomite for use as a bed material in pressurized oxygen/steam blown fluidized bed gasification of biomass, it is important to understand how the material properties influence the mechanical integrity under the conditions present in pressurized fluidized bed gasifiers.

Fragmentation of dolomite particles during calcination is extensively reported in the literature [8,17]. The poor mechanical strength of calcined dolomite is a problem, hindering its use in some reactor types, since larger fluxes of eroded small particles could plug pipes in heat exchangers or deactivate catalysts located in downstream processes, as well as lead to large amounts of fine fly ash particles, potentially, resulting in undesired amount of waste. Javier Gil et al. [8] carried out biomass gasification tests with air in a fluidized bed using dolomite mixed with silica sand as bed materials. The superficial gas velocity had an obvious effect on the elutriation rate, indicating that calcined dolomite is very soft and easily breaks up into particles with a wide particle size distribution. The calcination process is the first step in the fragmentation process and is of major concern when striving to minimize the loss of bed material. Since CaO, formed during calcination of the dolomite at elevated temperatures, can act as an effective catalyst in tar cracking [8–14], the bed temperature, therefore, need to be above the calcination temperature, but meanwhile below the temperature,

* Corresponding author.
E-mail address: chunguan@kth.se (C. Zhou).

http://dx.doi.org/10.1016/j.fuproc.2016.11.017
Received 2 September 2016; Received in revised form 17 November 2016; Accepted 18 November 2016
Available online 08 August 2017

triggering agglomeration in fluidized beds. However, in view of the mechanical strength of dolomite bed materials, a bed temperature below the calcination temperature is preferred, because fresh dolomite has a higher strength, compared to the much softer fully calcined dolomite [8]. Another important parameter is the pressure, where a higher-pressure results in a higher partial pressure of CO_2, preventing a full calcination or enabling a re-carbonation of the dolomite. Thus, dolomite in a pressurized gasification system could have a better mechanical integrity, compared to a corresponding use in an atmospheric gasification system.

Dolomite minerals have different chemical and physical properties, which almost certainly influence the mechanical integrity during use. Dolomite is a sedimentary rock and the chemical and physical properties vary by region. Dolomites are generally formed through a process known as dolomitisation, involving a reaction between limestone and Mg^{2+} in seawater or subsurface fluids of marine or meteoric origin. However, many existing dolomites are assumed to be alternation products of preexisting dolomite phases after metamorphism rather than being originally formed, so-called unaltered dolomites [18]. Dolomites subjected to metamorphism generally experience a transformation from finely to coarsely crystalline mosaics of either planar or non-planar texture, which corresponds to a change of the dolomite crystal size distribution from unimodal to a lognormal distribution. As reported by Kushnir et al. [19], fine-grained calcite-dolomite composites are apt to deform by grain boundary sliding assisted by diffusion creep and possible limited dislocation glide. Component crystals in neomorphic dolomites have highly irregular intercrystalline boundaries (may be curved, lobate, serrated, or indistinct), which can increase the mechanical strength of dolomites. The transformation from finely to coarsely grained dolomite changes the porosity, which may be a factor affecting the calcination process, due to its influence on the mass transfer of gaseous species [20]. Some studies have concluded the dolomite's superiority over limestone as a CO2 sorbent and revealed the mechanisms by comparing the differences of their textural properties [21–27]; however, most of these studies focused on the roles of MgO in preventing the deactivation of CO2 sorbents. So far relatively little attention has been given to how the difference in dolomite chemical and physical properties affects the calcination behaviour and the mechanical strength after calcination.

The present study is part of larger work aimed at gaining insights into dolomite behaviors in pressurized bubbling fluidized bed gasification of biomass. At present, most of the studies published on biomass gasification in fluidized beds focus on bed materials tar cracking ability and anti-agglomeration potentialities, which are also the main concerns for its industrial application. The tar cracking abilities of dolomite which has been extensively investigated in case of atmospheric fluidized bed gasification, or for downstream secondary catalysis conversion, as already mentioned above [13,14]. Dolomite materials ability to function as a tar cracking bed material under pressurized conditions is still not elucidated, but is not the scope of the present study and will be saved for the future. The present study aims at presenting our work mainly focusing on how to select a proper dolomite for use in a pressurized biomass bubbling fluidized bed gasifier in connection to its mechanical integrity. The poor mechanical strength of dolomite during atmospheric fluidized bed combustion/gasification has been studied and reported [8]. Nevertheless, the stability of dolomite at pressurized conditions in a fluidized bed gasifier has, to the best of our knowledge, so far not been investigated. The stability of dolomite in a pressurized fluidized bed gasifier, depending on a dolomite materials properties, are investigated for the first time. Two types of dolomite with different chemical and physical properties were investigated, examining the fragmentation due to mechanical strength, as well as pores network and structures under pressurized conditions. The corresponding change of micro-structure, occurring as the dolomite chemical transforms in the reactor, was further inspected. A specific objective was to propose criteria for dolomite selection for pressurized fluidized bed gasification.

Table 1
Chemical properties of bed materials.

Content (% db)	Glanshammar	Sala
CaO	30.2	30.2
MgO	20.5	20.6
Al_2O_3	0.43	0.60
SiO_2	3.3	3.6
TiO_2	0.007	–
Fe_2O_3	0.49	0.50
K_2O	0.07	–
Na_2O	0.20	–
MnO	0.10	–
P_2O_5	0.02	–
NiO	–	–
Sum of oxides	55.317	55.50
Loss on ignition (LOI)	44.5	44.0

2. Methods

2.1. Dolomite properties

Two types of dolomite, Glanshammar and Sala dolomite, were used as bed materials. The main components are shown in Table 1, indicating Glanshammar and Sala having similar quantities of CaO, MgO, and SiO_2.

2.2. Fuel feedstock

Both the Glanshammar and Sala dolomite were tested in a pressurized bubbling fluidized bed gasifier using pine pellets with a diameter of 3 mm as fuel feedstock. For comparison, the Glanshammar dolomite was also tested, using another type of fuel, birch chips. The proximate and ultimate analysis of fuel materials is shown in Table 2.

2.3. Setup

The experiments were carried out in a pilot scale bubbling fluidized bed gasifier at KTH Royal Institute of Technology. A schematic is shown in Fig. 1. The unit consists of a steam generator, a feeding hopper, and a pressurized fluidized bed reactor followed by a high-temperature filter and a secondary reformer reactor. The main technical data of the reactor and a detailed description of the experimental procedure are presented elsewhere [7].

2.4. Experimental procedures

The sieved bed material, see Table 3 for the particle size, is loaded as a raw mineral into the reactor before the heating up and pressurizing of the reactor. Two streams of steam, one originating directly from the steam generator and another stream passing the outer reactor wall of the freeboard to prevent overheating in the freeboard, before entering

Table 2
Proximate and ultimate analysis of tested material.

Proximate analysis	Unit	Pine	Birch
Moisture content at 105 °C	%	6.0	6.7
Ash content, 550 °C db	% (dry)	0.41	< 0.30
Volatile matter, 900 °C	% (dry)	82.4	85.6
Fixed carbon (calculated)	% (dry)	17.2	14.1
Ultimate analysis (dry composition)	Symbol	Pine (%)	Birch (%)
Sulfur	S	< 0.012	< 0.012
Carbon	C	47.7	49.0
Hydrogen	H	6.1	6.0
Nitrogen	N	0.16	0.18
Oxygen	O	43.0	44.4
Chlorine	Cl	0.03	0.01