Fuel 154 (2015) 217–221

Contents lists available at ScienceDirect

Fuel

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

Improving the kinetics of the CO_2 gasification of char through the catalyst/biomass integration concept

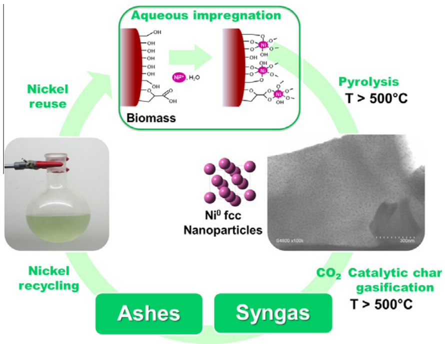
Yohan Richardson [a,*], Séverin Tchini Tanoh [a], Anne Julbe [b], Joël Blin [a,c]

[a] Biomass Energy and Biofuels Laboratory (2iE/CIRAD), International Institute for Water and Environmental Engineering, 1, Rue de la Science, 01 BP 594 Ouagadougou, Burkina Faso
[b] Institut Européen des Membranes (IEM), UMR 5635 CNRS-ENSCM-UM2, Université Montpellier 2 (CC 47), Place Eugene Bataillon, F-34095 Montpellier Cedex, France
[c] Biomass, Wood, Energy, Bioproducts Unit (BioWooEb), French Agricultural Research Centre for International Development (CIRAD), B-42/16, 73, Avenue J.-F. Breton, F-34398 Montpellier Cedex 5, France

HIGHLIGHTS

- The interest of the catalyst/biomass integration concept is highlighted in biomass char gasification.
- Kinetics of CO_2 gasification of char was substantially improved by the Ni^0 nanoparticles embedded in the carbon matrix.
- Both Ni^0 NPs formation and CO_2 gasification of the nickel char nanocomposite can occur at 500 °C.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 January 2015
Received in revised form 20 March 2015
Accepted 24 March 2015
Available online 31 March 2015

Keywords:
CO_2 gasification
Process intensification
Catalyst integration
Nickel nanoparticles

ABSTRACT

The catalyst/biomass integration concept is demonstrated to promote the reduction of char residence time and/or energy consumption through the catalysis of the rate limiting step of the whole biomass gasification process. Both the in-situ formation of the Ni^0 nano catalyst and the CO_2 gasification of the resulting nanocomposite char/nanoNi^0 can occur at temperatures as low as 500 °C.

1. Introduction

Development and implementation of biorefining processes is currently considered as the main keystones for the establishment of a sustainable bio-based economy [1–3]. Given the economic context of most worldwide regions, the future integrated biorefineries would be small to medium scale and thereby need for small and smart technologies affording high biomass feedstock flexibility [4]. Process intensification and catalysis are considered as one of the keys concepts in the development of these core biorefining technologies [4–7]. In this context, emerging intensification approaches are being considering and consist of different strategies of catalyst integration that target both reduction of biomass residence time in the gasification reactor and simplification of downstream syngas treatment before its subsequent catalytic conversion [6]. Two different strategies can be considered: (i)

---

* Corresponding author. Tel.: +226 77 01 13 73; fax: +226 25 49 28 01.
E-mail addresses: richardson.yohan@gmail.com, yohan.richardson@2ie-edu.org (Y. Richardson).

http://dx.doi.org/10.1016/j.fuel.2015.03.059
0016-2361/

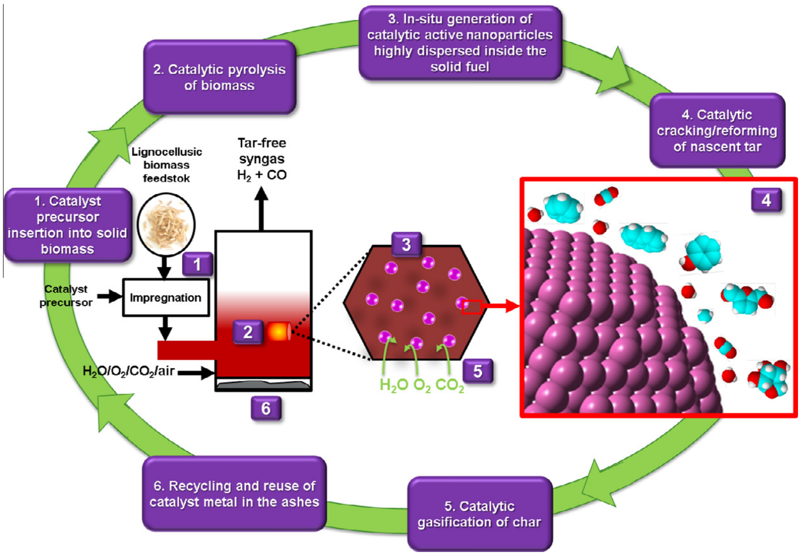


Fig. 1. The concept of catalyst/biomass integration applied to biomass gasification developed by our group (adapted from [11]).

catalyst/reactor integration through the development of new catalytic microreactors or microstructured catalysts [8–10], and (ii) catalyst/biomass integration through the development of a new concept of integrated catalytic biomass gasification [6]. The catalyst/biomass integration strategy is being developed by our group as an alternative process intensification approach to the highly expensive noble metal-based catalytic microreactors and lead to new concept of integrated catalytic biomass gasification, illustrated in Fig. 1 [6,11]. This concept relies on the postulate that heterogeneous catalysts, used to convert solid lignocellulosic biomass directly into syngas, can be made substantially more efficient by improving the catalyst/biomass contact. Indeed, unlike petroleum hydrocarbons, solid biomass particles do not easily interact with a solid catalyst and high temperatures are needed to compensate for the weak catalyst/biomass contact [12]. The achievement of a closer contact between a catalyst and lignocellulosic biomass targets (i) a change in the mechanisms of the first biomass decomposition stages leading to high selectivity for a given product and (ii) an substantial improvement in catalyst efficiency for solid fuel conversion, enabling the use of lower temperatures and/or shorter reaction times. Our concept of integrated catalytic biomass gasification consists of inserting the catalyst metal precursor into the lignocellulosic biomass feedstock during an impregnation stage with aqueous solutions of transition metal salts, promoting wide dispersion of the precursor inside the lignocellulosic matrix. The catalytic active phase as metal or metal oxide nanoparticles is then in-situ generated, inside the feedstock, during the thermochemical conversion. As highlighted in Fig. 1, this concept comprises different key reaction steps including (i) catalyst precursor insertion into solid biomass, (ii) catalytic pyrolysis of biomass and its main macromolecular constituents, (iii) in-situ generation of catalytic active nanoparticles highly dispersed inside the solid fuel, (iv) catalytic conversion of nascent tar over the freshly formed nanoparticles, (v) catalytic gasification of the nanocomposite char residue and (vi) recycling and reuse of the catalyst metal species maintained in the ashes. Each of these reaction steps requires a fundamental understanding in order to further develop a new high-efficiency, small-sized gasification process. Indeed, a fundamental understanding of the biomass catalytic thermochemical conversion processes at nanoscales is critical to develop new breakthrough conversion technologies leading to the design of the future intensified gasification processes. Specifically, the knowledge at nanoscales of the behavior of catalyst-derived transition metal species during impregnation, pyrolysis, gasification and recycling is crucial for the development of this integrated catalytic biomass gasification concept. Our approach is thus to first study each of these reaction steps from fundamental material chemistry, catalysis and biomass thermochemistry standpoints, in order to develop an intensified catalytic gasification reactor based on nanoscale control of catalytic reactions and catalyst lifecycle. This concept has been illustrated using a nickel catalyst precursor in previous work in which the occurrence of in situ formation of nickel metal nanoparticles during biomass pyrolysis in the temperature range 400–500 °C was demonstrated [13]. Fundamental issues regarding mechanisms involved in biomass impregnation with the metal precursor [11,13], formation of the nickel metal nanoparticles [13], primary and secondary catalytic pyrolysis of biomass and its making up macromolecules [11,14], have been addressed in previous works. The purpose of this communication is to provide some recent catalytic results that demonstrate the potential of this catalyst/biomass integration strategy for process intensification in the production of syngas, by addressing the rate limiting reaction step of the whole biomass gasification process: the CO_2 gasification of the char residue.

2. Experimental

The biomass feedstock used was beech wood, conditioned in the form of chips screened between 1.4 and 1.6 mm. 50 g of beech wood chips previously dried at 105 °C for 1 h, were impregnated with a nickel nitrate aqueous solution by a vacuum impregnation method described previously [11]. The corresponding impregnated biomass samples were called #Bx, where x was the metal content in the biomass sample determined by ICP-OES, expressed in mol kg^{-1} of dried nickel-free (dnf) biomass. A blank sample prepared in the same conditions using a metal-free aqueous solution was called #B0. In order to compare the catalytic effect of in-situ generated Ni^0 nanoparticles with the catalytic effect of preformed Ni^0 nanoparticles, Ni^0 nanoparticles beforehand synthesized by a microwave-assisted polyol method described elsewhere [15], were directly inserted according to a method previously developed and described in [11]. These samples were called #BNi^{0}x (where x was the metal content in the wood determined by ICP-OES, expressed in mol kg^{-1} of dnf wood). In order to demonstrate the technical feasibility of the catalyst recycling in the catalyst/biomass integration concept, a