Ni and Ni-Fe perovskite for catalytic abatement of tar

C. Gervasio, E. Grieco and G. Baldi

Abstract

Gasification is one of the more promising techniques to produce energy from biomass. One of the major problem to be solved in the application of this technology is the hot gas cleanup from tar. Tar is a complex mixture of hydrocarbons and oxygen containing compounds having a molecular weight higher than benzene and condensable at room temperature. Tar is an undesired product because it leads to the formation of aerosol and the deposition inside the process equipment such as gasifier, piping, engine or turbine system that causes mechanical problems [1]. The composition of tar depends on pyrolysis conditions [2]. Tar elimination can be made afterwards the gasifier (secondary methods) through scrubbing operation with H_2O or organic liquids, thermal or catalytic cracking. A convenient choice of the operational parameters, appropriate modifications in the project of the gasifier and the use of a suitable catalyst inside the bed of the gasifier can assign to secondary methods prevailingly the role of polishing with a clear economic saving. In fact to produce liquid fuels (Fischer-Tropsch process) it is necessary to reduce the concentration of tar in the syn-gas to very low values (10^{-3} or 10^{-4} g/Nm^3). Among secondary methods catalytic cracking is the most promising way to eliminate tar [3]. Actually there are many types of catalysts used for this application: minerals like calcined rocks, olivine, clay minerals and iron ores or synthetic catalysts like zeolites, activated alumina, alkali metal-based or transition metal based catalysts. In particular Ni-based catalysts are 8-10 times more active than dolomite, are able to attain complete tar elimination at 900°C and to increase the yield of CO_2 and H_2. The problem is their rapid deactivation due to sulphur and high tar content in the feed [4]. As suggested by S. Rapagnà et al. [5] to limit the problem of rapid deactivation we have chosen to use Ni-based perovskite type oxides. In fact perovskites are well defined structures with high metallic dispersion and a strong interaction between the elements included in the structure that limit the sintering of the active specie and carbon build-up. To inhibit the coking is necessary that the clusters of the active metal remain of a dimension smaller than a certain critical size [6]. Perovskites are characterised by oxygen mobility and they are also stable in a non-stoichiometric structure that improve their catalytic activity.

We have carried out our tests in a laboratory plant. Two gas chromatographs were used to analyze cracking reaction products. Naphthalene and n-exadecane were chosen as representative tar compounds; according to Roberto Coll et al. [7] naphthalene is one of the most stable tar compounds. $LaNiO_3$ and $LaNi_{0.3}Fe_{0.7}O_3$ have been tested as catalyst for tar cracking reaction. They have been prepared by thermal low-temperature decomposition of La, Ni and Fe nitrates, characterised by BET, XRD and EDS analyses and tested in a laboratory reactor at 500-600°C. The tests on $LaNiO_3$ show that it has a very high activity but XRD characterisation reveals that the catalyst is not stable in the reducing atmosphere produced during the cracking tests. XRD and EDS analysis show that there is carbon deposition on catalyst that mechanically blocks the passage of flow. To try to limit the problem of reduction of nickel we have introduced iron in the perovskite structure. On the basis of the tests made by Proviender at al. [8] we have chosen to test $LaNi_{0.3}Fe_{0.7}O_3$ because it seems to provide a good compromise between catalytic activity and stability under reaction conditions. The addition of iron in the catalyst structure is effective only for the n-exadecane cracking reaction. In the tests with naphthalene $LaNi_{0.3}Fe_{0.7}O_3$ does not solve the problem of carbon deposition on catalyst and hence its deactivation.

[1] J. Srinakruang, K. Sato, T. Vitidsant, K. Fujimoto, "Highly efficient sulfur and coking resistance catalysts for tar gasification with steam", Fuel 2006, Vol. 85, pp. 2419–2426.

[2] T.A. Milne, N. Abatzoglou, R.J. Evans, Biomass gasifier ''tars'': their nature, formation and conversion. National Renewable Energy Laboratory (NREL), reports NREL/TP-570-25357, Colorado, 1998.

[3] Umberto Arena, Ugo Leone, Maria Laura Mastellone, "Recupero di energia e materia da rifiuti solidi: i processi le tecnologie, le esperienze, le norme", AMRA S.c. a r.l. Sezione Politiche Territoriali, Facoltà di Ingegneria e Facoltà di Scienze Ambientali, Seconda Università di Napoli, p. 178

[4] Z. Abu El- Rub, E. A. Bramer, G. Brem, "Review of Catalysts for Tar Elimination in Biomass Gasification", Ind. Eng. Chem. Res. 2004, Vol. 43, pp. 6911-6919.

[5] S. Rapagnà, H. Provendier, C. Petit, A. Kiennemann, P. U. Foscolo, "Development of catalysts suitable for hydrogen or syn-ges production from biomass gasification", Biomass & Bioenergy 2002, Vol. 22, pp. 377-388.

[6] J. Guo, H. Lou, Y. Zhu, X. Zheng, "La-based perovskite precursors preparation and its catalytic activity for CO_2 reforming of CH_4", Materials Letters 2003, Vol. 57, pp. 4450-4455.

[7] R. Coll, J. Salvao´, X. Farriol, D. Montane˙, "Steam reforming model compounds of biomass gasification tars: conversion at different operating conditions and tendency towards coke formation", Fuel processing Technology 2001, Vol. 74(1), pp. 19–31.

[8] H. Proviender, C. Petit, C. Estournès, S. Libs, A. Kiennemann, "Stabilisation of active nickel catalysts in partial oxidation of methane to synthesis gas by iron addition", Applied Catalysis A: General 1999, Vol. 180, pp. 163-173.