



Investigation of competitive COS and HCN hydrolysis reactions upon an industrial catalyst: Langmuir–Hinshelwood kinetics modeling



David Chiche*, Jean-Marc Schweitzer

IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

ARTICLE INFO

Article history:

Received 7 September 2016

Received in revised form

24 November 2016

Accepted 1 December 2016

Available online 5 December 2016

Keywords:

Synthesis gas

Purification

Kinetics modeling

Catalytic conversion

Titania

ABSTRACT

Distinct and simultaneous COS and HCN hydrolysis reactions over an industrial TiO₂ based catalyst were extensively studied in this work in the scope of synthesis gas purification applications. 144 experiments were carried out, including 92 experiments that allowed to achieve partial conversion rates and showed reaction kinetics sensitivity to operating parameters. Significant crossed influences were evidenced between both COS and HCN hydrolysis reactions. The concomitant occurrence of both reactions showed to detrimentally affect each other upon COS and HCN conversion rates, and therefore upon kinetic rates. This was explained through a competitive adsorption of HCN and COS reactants upon catalyst surface active sites. Inhibition of catalytic activity by the presence of NH₃ and H₂O was also evidenced and explained through competitive adsorption phenomena. For the operating conditions ranges explored, H₂S and CO₂ had no sensitive impact on the kinetics of the COS and HCN hydrolysis reactions. However, the moderate impact of CO₂ upon COS and HCN conversion rates might be explained by the large CO₂ excess compared to COS and HCN levels. A reaction model has been fully developed considering hydrodynamic, external mass transfer and intra particle diffusion limitations, and Langmuir–Hinshelwood reaction mechanisms for both COS and HCN hydrolysis reactions. Langmuir–Hinshelwood kinetic rate laws were indeed considered to account for the detrimental effect of gaseous species upon COS and HCN conversion kinetic rates, through competitive adsorption upon catalyst active sites of COS, HCN, H₂O, and NH₃. Collected kinetic data as a function of reactor size, gas residence time, temperature and reactants partial pressures were used to validate and fit kinetic and adsorption constants. Very good agreement was achieved between experimental and calculated COS and HCN conversion rates from the model developed, that allowed complete validation of the Langmuir–Hinshelwood based modeling. The coupled hydrodynamic–reaction model also constitutes a complete industrial reactor model taking into account all the potential limitations, and can be used as a powerful predicting tool for industrial process design, *i.e.* fully usable for industrial process scale-up and optimization purposes.

© 2016 Elsevier B.V. All rights reserved.

Abbreviations: A_p (m²), particle surface area; α_i , thermodynamic parameter; β_i , thermodynamic parameter; T (K), temperature; b_{COS} (bar⁻¹), COS adsorption constant; b_{HCN} (bar⁻¹), HCN adsorption constant; b_{NH_3} (bar⁻¹), NH₃ adsorption constant; $b_{\text{H}_2\text{O}}$ (bar⁻¹), H₂O adsorption constant; C_i^g (mol m⁻³), gas concentration of compound i ; C_i^p (mol m⁻³), particle concentration of compound i ; D_{ax}^g (m² s⁻¹), gas axial dispersion coefficient; $D_{\text{eff},i}$ (m² s⁻¹), effective diffusion coefficient; d_p (m), particle diameter; D_m (m² s⁻¹), molecular diffusion coefficient; E_1 (J mol⁻¹), activation energy of reaction 1; E_2 (J mol⁻¹), activation energy of reaction 2; k_1 (SI), kinetic constant of reaction 1; k_2 (SI), kinetic constant of reaction 2; k_{gs} (m s⁻¹), gas–solid mass transfer coefficient; $K_{\text{eq},i}$, i^{th} thermodynamic constant; L_c (m), particle characteristic length; m_T , Thiele modulus; P_{COS} (bar), COS partial pressure; P_{CO_2} (bar), CO₂ partial pressure; $P_{\text{H}_2\text{S}}$ (bar), H₂S partial pressure; P_{HCN} (bar), HCN partial pressure; P_{CO} (bar), CO partial pressure; $P_{\text{H}_2\text{O}}$ (bar), H₂O partial pressure; P_t (bar), total pressure; Re, Reynolds number; r_1 (mol s⁻¹ kg⁻¹), reaction rate of reaction 1; r_2 (mol s⁻¹ kg⁻¹), reaction rate of reaction 2; R (J mol⁻¹ K⁻¹), ideal gas constant; r (m), radius coordinate; R_p (m), particle radius; Sc, Schmidt number; Sh, Sherwood number; V_p (m³), particle volume; v_{sg} (m s⁻¹), superficial gas velocity; z (m), reactor elevation; ΔH_{COS} (bar⁻¹), COS adsorption enthalpy; ΔH_{HCN} (bar⁻¹), HCN adsorption enthalpy; ΔH_{NH_3} (bar⁻¹), NH₃ adsorption enthalpy; $\Delta H_{\text{H}_2\text{O}}$ (bar⁻¹), H₂O adsorption enthalpy; ε_g , gas holdup; ε_s , solid holdup; ε_p , particle porosity; δ (m), film thickness; $\mu_{i,j}$, stoichiometric coefficient; ρ_g (kg m⁻³), gas density; ρ_s (kg m⁻³), solid density; τ , residence time; τ_p , particle tortuosity.

* Corresponding author.

E-mail address: david.chiche@ifpen.fr (D. Chiche).

<http://dx.doi.org/10.1016/j.apcatb.2016.12.002>

0926-3373/© 2016 Elsevier B.V. All rights reserved.

1. Introduction

To protect the environment and preserve natural resources, a more diverse energy mix is essential, especially in the transportation industry. As the only liquid fuels that can be used to supplement fossil based transportation fuels, biofuels play a major role in the diversification process.

Some research is currently focusing on the development of second-generation biofuels that can be made from non-edible, ligno-cellulosic materials derived from wood, straw, forest wastes, and dedicated crops [1,2]. By using the non-edible part of plants, second-generation biofuels are expected to enable to meet growing biofuel needs without competing with food production. In addition, they can use raw materials that are in abundant supply and deliver an interesting environmental performance. Second-generation biofuels can be produced from biochemical and thermochemical routes. Especially, as shown in Fig. 1, thermochemical conversion consists in the gasification of carbonaceous feedstocks under partially oxidizing atmosphere into a synthesis gas (or syngas) composed of a CO-H₂ mixture [3]. After multiple gas conditioning steps aimed at reaching the required specifications (H₂/CO ratio adjustment and CO₂ removal) [4,5], the syngas undergoes the Fischer-Tropsch reaction in order to produce synthetic liquid fuel [6–8]. However, synthesis gas also contains various impurities that must be removed in order to prevent Fischer-Tropsch catalyst poisoning [9–13].

Integrated Gasification Combined Cycles (IGCC) power generation processes also constitutes more efficient and cleaner alternative technology for future energy production [14–16]. As for XTL based Fischer-Tropsch technology, this technology is also based on a first step of feed gasification into a synthesis gas. In IGCC power plants, the syngas is burnt into a gas turbine to produce electrical energy. Synthesis gas impurities such as H₂S, COS and HCN, mixed to H₂, are responsible for the corrosion of the industrial units [17], especially the combustion turbine blades used in IGCC processes.

Among the impurities present in synthesis gases, significant amounts of sulfur and nitrogen compounds are expected whatever the kind of feedstock (fossil or biomass), which are known to be severe poisons for Fischer-Tropsch catalysts [9,10,12,18], and responsible for the corrosion of industrial equipments [17].

Sulfur compounds should be present in the synthesis gas as H₂S and COS, also depending on the gasification process operating conditions [3,11]. The presence of organic species such as mercaptans and thiophenic compounds in synthesis gases obtained from coal

gasification is also reported [3]. It however may occur for gasification processes operating at low temperature (fixed or fluidized bed). In gasification processes operating at temperature higher than 1400 °C such as entrained flow reactor, sulfur is only present in the synthesis gas as H₂S and COS, and no organic sulfur compounds should be found downstream according to thermodynamic calculations. Biomass feedstocks generally exhibit a much lower sulfur content than fossil feedstocks (coal, petcoke) [3,11,19,20]. Syngas H₂S and COS contents may thus vary from hundreds to thousands of mol ppm as a function of the feedstock.

Nitrogen species present in the feedstocks are converted into HCN and NH₃ in the gasification process. According to literature, the NH₃/HCN ratio depends on many parameters [21–24], such as the nature of feedstocks (that may contain nitrogen compounds with different speciation), operating conditions of the gasification process such as pressure and temperature, gasification process technology (fixed bed, fluidized bed, entrained flow reactor). Nitrogen feedstock contents may vary from 0.1 to 3.3 wt.% [11,25–27], which affect accordingly the resulting nitrogen syngas contents after the gasification step [28]. In the gasification process, HCN formation is predominant from aromatic nitrogen compounds found in fossil feedstocks, whereas combustion of aminoacids and other nitrogen species usually present in biomass predominantly leads to the formation of NH₃ [3,11,22]. Syngas HCN contents may vary from a few mol. ppm to hundreds of mol ppm, and NH₃ contents from a few mol ppm to 14000 mol ppm [3,11]. Other nitrogen compounds might also be present in synthesis gases such as isocyanic acid HNCO, and nitrogen oxides NO_x, also depending on the gasification operating conditions and technology [3,11].

Among existing purification technologies for COS and HCN removal [13,29,30], catalytic processes attract a great deal of interest. Indeed, both COS and HCN impurities can undergo hydrolysis reactions that are thermodynamically highly favored at low temperature. COS and HCN hydrolysis reactions can respectively be written as follows:



Catalysts are however required to improve both reactions kinetics. Regarding COS hydrolysis, most studied catalysts in the literature are metal oxides such as TiO₂, Al₂O₃, ZnO and ZrO₂ [13,31–33]. Especially, catalyst activity seems to be related to catalyst surface basicity [34,35]. Alumina and TiO₂ supported catalysts, such as those used as catalysts in Claus processes, are also used for the COS conversion into H₂S. Considering the activation energy, gamma alumina materials might be more active than TiO₂ materials [34,36], and should thus favor COS hydrolysis from lower temperature ($T < 200$ °C). However, experimental observations evidence water inhibition on gamma alumina materials, occurring through a competitive adsorption on catalyst surfaces which results in a reduction of catalytic activity. As low water contents usually result in an increase of COS conversion, water inhibition effect is reported to occur above a certain H₂O partial pressure, which also depends on COS partial pressure and temperature [33,37,38]. These effects have also been observed on other catalysts such as titania materials. For example, this has been reported in a comparative study on commercial catalysts based on alumina (Kaiser-201, Kaiser Aluminum and Chemicals) and titania (CRS 31, Axens) [36]. Alumina materials, which exhibit relatively high hydrophilic properties, seem to be more affected by catalytic inhibition by water than TiO₂ based materials. Therefore, under operating conditions close to industrial conditions, TiO₂ based catalysts seem to be more active than alumina catalysts. Temperature increase results in a diminution of catalytic inhibition to water, as this favors both kinetic rate

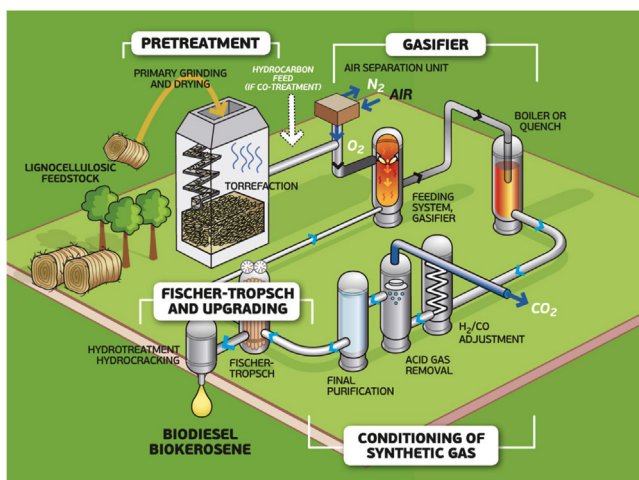


Fig. 1. Schematic representation of the second-generation biofuels production chain from B-XTL thermochemical routes. (source IFPEN).

Download English Version:

<https://daneshyari.com/en/article/6454304>

Download Persian Version:

<https://daneshyari.com/article/6454304>

[Daneshyari.com](https://daneshyari.com)