



Glycerol steam reforming with low steam/glycerol ratio in a two-zone fluidized bed reactor

Miriam Yus, Jaime Soler, Javier Herguido, Miguel Menéndez*

Catalysis, Molecular Separations and Reactor Engineering Group (CREG), Aragon Institute of Engineering Research (I3A), Universidad de Zaragoza, Mariano Esquillor s/n, 50018 Zaragoza, Spain

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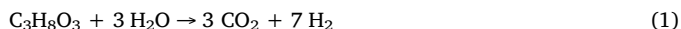
ABSTRACT

The production of hydrogen from glycerol steam reforming has been studied in several reactors. In conventional reactors the catalyst is deactivated by coke: in fixed bed reactors plugging was observed if a low steam/glycerol ratio was employed, while in fluidized bed reactors it was possible to operate for a longer time-on-stream. The use of a two-zone fluidized bed reactor is studied in this work, as a method to counteract the problem of catalyst deactivation by coke. The glycerol reforming takes place in the upper part of this reactor while the catalyst is simultaneously regenerated in the lower part, where a stream of a regenerating gas is introduced. It has been found that CO₂, O₂ or H₂O can act as regenerating gas in a two-zone-fluidized bed reactor, allowing steady state operation at a water:glycerol molar ratio as low as 1.25. The effect of the operating conditions has been studied and the yield to the main products was compared with the calculated values assuming thermodynamic equilibrium.

1. Introduction

Glycerol is obtained as a by-product from the manufacture of biodiesel, representing approximately 10 wt% of the production. The large increase in biodiesel production worldwide in recent decades [1] has caused an oversupply of glycerol which the market has not been able to absorb. The price of crude glycerol has dropped as low as 50\$/t [2]. This situation provides the motivation to find new uses. Although glycerol is already employed in many applications, the large amount produced as a byproduct of biodiesel (c.a. 3 million tons of glycerol per year) requires a use that can absorb this gigantic production, which is not the case for high value chemicals or health care products. One possibility is hydrogen production. Hydrogen is employed in very large quantities in many applications, and syngas (the mixture of CO and H₂) can be transformed by several known techniques (e.g. methanol synthesis or the Fischer Tropsch process) into liquid fuels, suitable for transportation.

Given this situation, it is not surprising that a growing number of researchers have embarked on the study of the glycerol reforming process, i.e. the production of hydrogen or syngas from the reaction of glycerol with water, according to the reaction:



The above reaction is produced simultaneously with several others, as

shown in Table 1. In fact, it is a combination of several elemental steps. This process can be considered analogous to the steam reforming of methane, widely employed in the industry to produce hydrogen, but using a renewable fuel.

As in the process of methane steam reforming, nickel based catalysts are the most widely studied for the dry reforming of methane, although noble metals (Pt, Rh, Ir, Ru, Rh) have also been reported extensively in scientific literature. It may be expected that, as in the case of methane steam reforming, the use of noble metals would be too expensive for use in glycerol steam reforming on an industrial scale, and nickel based catalysts would be employed in practice.

Many studies of nickel based catalysts with a variety of supports have been reported in the literature. Table 2 shows a list of such works, including details of the amount of nickel in the catalyst, the type of support and the water/glycerol molar ratio (WGR) employed. One striking fact revealed in this list is the large number of researchers who have employed water/glycerol molar ratios equal to or larger than 6. According to Eq. (1) the stoichiometric ratio for hydrogen production is 3, and much lower ratios should be used if the target is to produce syngas. The explanation for the large water/glycerol ratio is the need to avoid coke deposition on the catalyst surface, which is usually quicker in the case of nickel rather than noble metal catalysts. However, the use of a large excess of steam would imply that a significant amount of the energy contained in the glycerol (or the equivalent amount from

* Corresponding author.

E-mail address: Miguel.menendez@unizar.es (M. Menéndez).

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Table 1
Most important secondary reactions occurring during glycerol steam reforming [3–5].

Reaction
$C_3H_8O_3 + 2 H_2 \leftrightarrow 2 CH_4 + CO + 2 H_2O$
$2C_3H_8O_3 + H_2 \leftrightarrow 3 CH_4 + 3 CO + 3 H_2O$
$C_3H_8O_3 + 5 H_2 \leftrightarrow 3 CH_4 + 3 H_2O$
$C_3H_8O_3 \leftrightarrow C_2H_4 + CO + 2 H_2O$
$CO + 3 H_2 \leftrightarrow CH_4 + H_2O$
$CO_2 + 2 H_2 \leftrightarrow 2 H_2O + C (s)$
$CO_2 + 4 H_2 \leftrightarrow CH_4 + 2 H_2O$
$CO_2 + CH_4 \leftrightarrow 2 CO + 2 H_2$
$CH_4 \leftrightarrow 2 H_2 + C (s)$
$C_2H_4 \leftrightarrow 2 H_2 + 2C (s)$
$2 CO \leftrightarrow C (s) + CO_2$
$C (s) + H_2O \leftrightarrow CO + H_2$
$C_2H_4 + H_2 \leftrightarrow C_2H_6$

Table 2
Ni based catalysts and water/glycerol molar ratio (WGR) employed by several authors.

%Ni	Support	T (°C)	WGR	Ref.
2–5	SiO ₂	350–450	46	[16]
2	Ce-Zr/Al ₂ O ₃	450–600	6	[17]
2.5	Ce/Al ₂ O ₃	600–900	6	[18]
4	Al ₂ O ₃	500–700	6	[19]
5	M-Ce/Al ₂ O ₃ (M = Pt, Ir, Pd, Ru)	700	6	[20]
5.1	Al ₂ O ₃	700	3	[21]
5–20	Al ₂ O ₃	400–600	3–12	[22]
5–20	Al ₂ O ₃ ; Al ₂ O ₃ -MgO	600	9	[23]
5.8	Al ₂ O ₃	600–700	16	[24]
7	SBA-15	600	6	[25]
7.8	LTA/CaO-LTA/MgO	600	9	[26]
9.6–12.7	CeO ₂ , MgO, TiO ₂	550–650	6–12	[27]
10	TiO ₂ , SBA-15, ZrO ₂	500–650	46	[28]
10	CeZrO	500–700	6–24	[29]
10	La ₂ O ₃ -SiO ₂	600	9	[30]
10	Al ₂ O ₃	600	24	[31]
10	Al ₂ O ₃ -MgO	600	9	[32]
10	Al ₂ O ₃ -CaO-MgO	750	9	[33]
12.6	La ₂ O ₃ -Al ₂ O ₃	500	46	[34]
12.6–13.4	Al ₂ O ₃ + (Mg, Ce, La, Zr)	600	507	[35]
13	CeO ₂ -Al ₂ O ₃	500–600	46	[36]
14.1	Al ₂ O ₃	400–700	9	[37]
14.1	Al ₂ O ₃	400–700	9	[38]
15	MgO, CeO ₂ , TiO ₂	550–650	6	[39]
15	Al ₂ O ₃	550	3–12	[40]
15	(K, Ca, Sr)-Al ₂ O ₃	600–800	9	[41]
15	CeO ₂	400–550	9	[42]
15	CeO ₂ -ZrO ₂	600–700	20–46	[43]
19–35	Al ₂ O ₃ /MgO	450–650	9	[44]
21–30	Al ₂ O ₃ , MgO, CeO ₂	800	9	[45]
23	LaAl ₂ O ₃	550	9	[46]
23–51	MgO, CuO/MgO, CuO/Al ₂ O ₃	150–650	> 9	[47]
57	SiO ₂	500–600	9–18	[48]

another fuel) would be employed simply to produce steam. This would be uneconomic in industrial applications, and therefore ways to reduce the steam/glycerol molar ratio are highly desirable. In fact the same could be said for most steam reforming processes, as is reflected in industrial efforts to decrease the steam/carbon ratio in methane steam reforming (e.g. [6,7]). Carbon deposition can cause a decrease in catalyst activity by encapsulation of metallic particles or coverage of the catalytic surface by amorphous coke. Under some conditions carbon whiskers are formed; although they do not produce a direct loss of activity, these whiskers can break the catalyst particles and block the gas flow in a fixed bed.

One way to reduce or even totally counteract the effect of coke formation in a catalytic reaction is the use of a Two-Zone Fluidized Bed Reactor (TZFBR). This device has been previously tested by our group for several reactions [8–10], showing that in many cases it is possible to

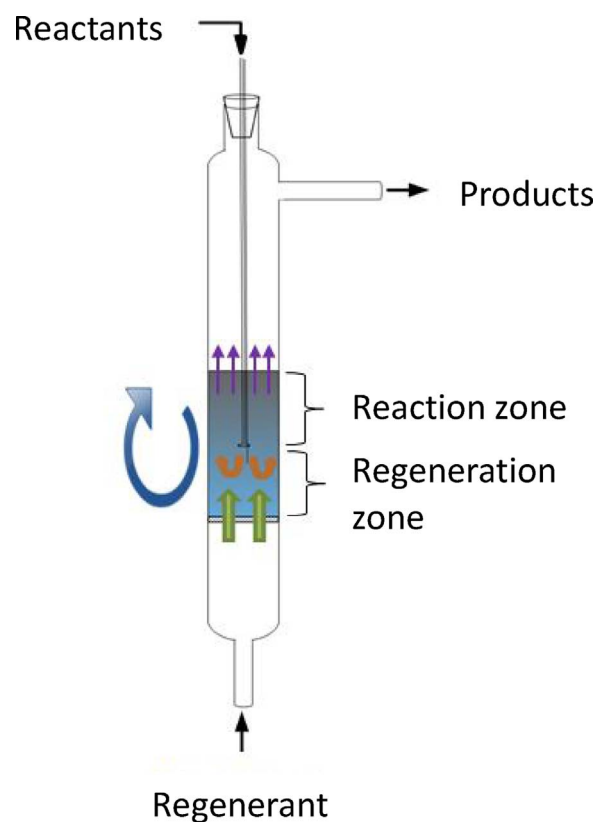


Fig. 1. Scheme of a Two-Zone Fluidized Bed Reactor (TZFBR).

achieve steady state operation under conditions where a conventional reactor would suffer catalyst deactivation. The use of a TZFBR has also been found to be beneficial for the oxidative coupling of methane by Talebizadeh et al. [11] and for oxidative dehydrogenation of butane by Rischard et al. [12] and has been proposed for glycerol dehydration to acrolein [13]. A scheme of a TZFBR is shown in Fig. 1. Two zones with different reaction environments are created in a fluidized bed by feeding two streams at two different points: a reacting gas (e.g. a hydrocarbon) is fed at an intermediate point of a fluidized bed of catalyst and a second gas for regeneration (e.g. oxygen) is fed at the bottom of the bed. The desired reaction (e.g. hydrocarbon reforming) is produced in the upper part of the bed and the catalyst regeneration occurs in the lower part. The continuous mixing of solid (caused by bubbles in a fluidized bed) transports the solid between both zones. In this way a dynamic equilibrium is achieved between coke formation in the upper zone and coke removal in the lower zone.

There is a clear incentive for the use of crude glycerol in this process, since its price is much lower than that of refined glycerol. The main problem for the use of crude glycerol could be the presence of salts (e.g. NaCl or Na₂SO₄) that would be deposited in the solid when the feed is vaporized. A potential advantage of using fluidized bed reactors could be that the inorganic salts found in crude glycerol would be deposited on the external surface of the catalyst, being easily removed by attrition and collected by external filters. This advantage has been found experimentally in a previous work [14,15] on the decomposition of crude glycerol for acrolein production.

This work aims to study the feasibility of using a TZFBR for glycerol reforming. In addition to some preliminary experiments in the absence of a catalyst and in a fixed bed reactor, the main part of the experimental work was devoted to comparing the performance of a conventional fluidized bed with that of a TZFBR. In addition, several regenerating gases have been studied in the TZFBR, including H₂O, O₂ and CO₂.

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