

Forced Composition Cycling of Propane Steam Reforming Using CO₂ as Carbon Gasifying Agent

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ABSTRACT

Recent investigation in our laboratory has shown that CO₂ is an effective carbon gasifying agent for the rejuvenation of coked metal catalysts [1]. A further advantage of using CO₂ over air (or oxygen) is the reduced possibility for catalyst sintering while serving as an avenue for minimizing greenhouse gas emission during operation. In this paper, we report the effect of periodic composition switching between propane steam reforming feed (H₂O/C₃H₈ mixture) and CO₂ in a fluidized bed reactor containing a Co-Ni catalyst. Experiments were conducted at a feed flow rate of 300 ml min⁻¹ with a low steam:carbon ratio (< 2) at 600C. Cycle period, τ , was varied between 5 to 20 minutes at different cycle split, s (0.5 and 0.8) using electrically actuated solenoid valves. Both H₂ and CO formation rates were higher (up to 5-fold and more than 10-fold respectively) than that attainable under steady-state operation at all periods investigated. Although the time-average H₂:CO ratio was lower than the steady-state equivalent, it was a function cycle period with a minimum at $\tau = 12$ minutes. This method of reactor operation presents a new and strategic way to tune product selectivity from hydrocarbon reforming for different downstream requirements with relative ease.

Keywords: Periodic operation, steam reforming, hydrogen production, catalyst regeneration

INTRODUCTION

The industrial production of synthesis gas - H₂/CO mixture - from hydrocarbon steam reforming is accompanied by unwanted coke deposition which ultimately leads to poor catalyst activity, selectivity and longevity. Coke removal may be achieved by the passage of a carbon gasifying agent over the catalyst bed. Conventionally, oxygen (or air) is used as the gasifying agent in industrial regenerators. However, in a recent publication, we have compared several carbon gasifiers and demonstrated that CO₂ is a more effective coke gasification agent than oxygen since it does not lead to catalyst sintering or other detrimental structural effects (Alenazey *et al.* 2008).

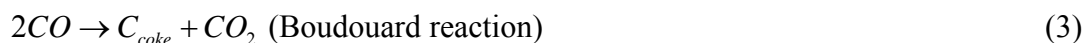
In this study, propane was used as the hydrocarbon substrate thus, the steam reforming reaction,



may be attended by coke formation via the dehydropolycondensation of chemisorbed hydrocarbon



or



where the empirical formula of the surface coke may be written as C_xH_{1-x} with $0 \leq x \leq 1$ depending on the H:C ratio in the coke.

In order to improve catalyst and reactor performance, this study proposes the periodic switching between the steam reforming operation and carbon gasification to minimize coking and hence increased time-average catalyst stability and longevity. Theoretical investigations of reactor dynamics within the past three decades suggest that the forced periodic composition cycling can lead to substantial improvements in both activity and product selectivity especially for reaction systems with nonlinear kinetics (Bailey, 1973; Schadlich *et al.* 1999; Gosiewski, 2000; Ayude *et al.* 2007). Experimental studies confirming these mathematical analyses have rapidly accumulated (Cutlip, 1979; Silveston, 1998; Opoku-Gyamfi *et al.* 2000; Marin *et al.*, 2008). Periodic composition and flow modulation have been used to improve the efficiency of catalytic reactors for air pollution control (Matros, 1990) while substantial rate improvements have been reported in a variety of chemicals syntheses (Adesina *et al.* 1986; Kiperman *et al.* 1999; Gosiewski, 2001; Velardi & Barresi, 2002; Larrando *et al.* 2001). Indeed, experimental validation has led to the development of commercial trickle-bed reactor for SO₂ oxidation that is more energy and resource-efficient in a sulphuric acid production plant (Bunimovich *et al.* 1995).

However, the control of catalyst deactivation via periodic composition cycling with a gasifying agent such as CO₂ has not been previously examined but has several interesting advantages, namely; (a) in-plant utilization of CO₂ (a greenhouse gas) leading to overall reduction in GHG emission from the petrochemical industries (b) minimisation and control of hot spot during catalyst regeneration with associated improvement in the physiochemical properties and longevity of the catalyst (c) increased time-average H₂ and CO formation rates since both species are generated during each section of the cycle albeit via different routes (d) flexibility in H₂:CO ratio permitting tunability to meet different downstream requirements e.g. in GTL fuels synthesis or ammonia or urea manufacture (e) reduction in reformer shutdown for catalyst revivification.

EXPERIMENTAL

Catalyst preparation and characterisation

The catalyst was prepared by double-impregnation of quantitative amounts of cobalt and nickel nitrates on thermally pre-treated γ -alumina (at 1023 K) to yield 5Co:15Ni/alumina wet solid. The latter was dried in an oven at 383 K overnight and subsequently calcined at 1023 K in air for 5 hours before crushing to 212-250 μ m particles employed in the propane steam reforming runs. Liquid nitrogen adsorption at 77 K on a Quantachrome

Autosorb-1 was used to determine the BET surface area and pore volume of both fresh and regenerated catalysts from different composition cycling runs. The organic content in the coked catalysts were obtained from a Shimadzu Total Organic Carbon Analyzer (model SSM-5000).

Reaction runs

The catalyst was initially reduced in flowing H₂ at 873 K for 2 hours in the quartz fluidised bed reactor (ID = 18 mm; 1g catalyst). Preliminary steady-state runs were carried out at 823 K using a feed containing steam:carbon ratio =1 at 300 ml min⁻¹ at normal temperature and atmospheric pressure. This composition was chosen to ensure carbon deposition during the reaction. Composition cycling runs were performed in the same reactor with alternate switching between the steam/propane/Argon feed and the 10%CO₂/Ar mixture. Periodic flow was controlled by three-way electrically-actuated solenoid valves connected to a computer-controlled timer to generate feed composition square-waves to the reactor. Cycle period, τ , is defined as the time interval between successive inputs of the same gas composition and hence the cycle split, s , is the fraction of the time spent in the steam/propane feed, t_1 to the total time spent under both CO₂ pulse and the steam/propane section. Accordingly,

$$\tau = t_1 + t_2 \quad (4)$$

$$s = t_1 / \tau \quad (5)$$

Four cycle periods ($\tau = 5, 10, 15$ and 20 minutes) were employed at each of two cycle splits ($s = 0.5$ and 0.8). Exit gas composition from the reactor was measured by on-line Shimadzu TCD-gas chromatograph (model 8A) equipped with a Haysep Q column. Instantaneous gas compositions were taken within each cycle over several cycles to guarantee the attainment of a cycle-invariant composition profile. Cycle-invariant state was typically achieved after about 150 minutes during periodic operation. The time-average rate, r_{cyc} , during a given cycle was computed from the instantaneous rate, r_i , within the cycle by,

$$\bar{r}_{cyc} = \frac{\int_0^{m\tau} r dt}{(m-1)\tau} \quad (6)$$

which for discrete data yields

$$\bar{r}_{cyc} = \frac{1}{\tau} \sum_{i=1}^N r_i \Delta t_i \quad (7)$$

where N is the number of data points within the cycle and Δt_i is the sampling interval.

RESULTS AND DISCUSSION

Table 1 shows the BET surface area and pore volume for both fresh and used catalysts. It is apparent that structural changes were relatively minor with less than 6% drop in surface area for the used catalysts although the reduction in surface area was larger for specimens obtained from runs with $s=0.8$. This is also consistent with the larger pore

volume reduction seen in catalysts employed for periodic operation experiments at $s=0.8$. Whilst both BET area and pore volume of the used catalysts appeared to decrease with period for runs at $s=0.8$, the results for the experiments with symmetrical split (0.5) do not manifest such a trend due to the relatively longer time spent in the cycle period for coke gasification thus ensuring better catalyst revivification closer to its original state.

Tab. 1 : Influence of cycle period and split on BET area and pore volume

Cycle period (min)	BET area (m^2g^{-1}) $s=0.5$	Pore volume (cc g^{-1}) $s=0.5$	BET area (m^2g^{-1}) $s=0.8$	Pore volume (cc g^{-1}) $s=0.8$
Fresh catalyst	144.6	0.556	----	-----
5	142.2	0.4897	144.4	0.458
10	144.3	0.4433	141	0.3320
15	143.7	0.5012	138.6	0.356
20	146.6	0.4566	136.8	0.314

Indeed, as may be seen in Table 2, the total organic carbon content values are generally higher for runs with a split of 0.8 while carbon residue was undetected (except at $\tau = 20$ mins) for runs with $s = 0.5$. Even so, values of the solid TOC content from both forced composition cycling runs were much lower than the carbon residue on the equivalent steady-state run measured at 59.1%. These data point to an extended longevity of the catalyst under periodic composition forcing rather than steady-state operation.

Tab. 2: Influence of cycle period and split on carbon content

Cycle Period (min)	% Carbon Content ($s=0.5$)	% Carbon Content ($s=0.8$)
5	0	9.991
10	0	21.85
15	0	22.97
20	5.555	29.5
Spent catalyst obtained under steady-state mode	59.09	59.09

Fig. 1 shows that the time-average H_2 production rate varies with cycle parameters and in particular, display an optimum at about $\tau = 12$ mins. Additionally, there is up to 5-fold increase in product formation rate under composition cycling compared to stationary-state run

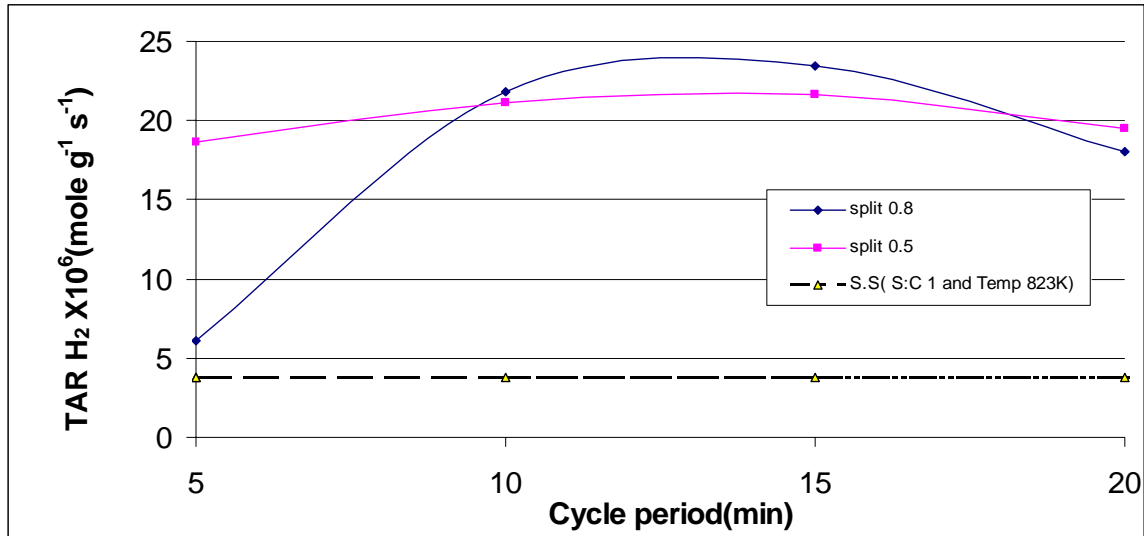


Fig 1: Effect of cycle period and split on H₂ formation
(TAR= time-average rate, \bar{r}_{cyc})

A similar behaviour is observed for time-average CO formation rate as evident from Fig. 2. The improvement in both H₂ and CO rates under periodic operation is due to the fact that these products are generated in each portion of the cycle. During the steam reforming partial cycle, H₂ and CO will be formed according to Eqn (1) while during coke gasification, these products will be formed via



where the empirical formula for coke, C_xH_{1-x} suggests that the carbonaceous layer may have widely different composition ranging from pure carbon (x =1) to surface hydrogen adatoms (x=0).

In the neighbourhood of the optimum period, (10 < τ < 15mins) H₂ and CO production rates were higher at s = 0.8 than at s = 0.5 due to the longer time spent in the steam reforming region than under CO₂ pulsing. However, at low cycle period (τ < 10 mins) the relatively short time spent renewing catalyst surface from carbon deposition did not appear to be sufficient compared to the length of time spent in the same cycle period, for s = 0.5. This will suggest that propane dehydrogenation proceeded at a much faster rate than CO₂ gasification of the deposited carbon. By same token, at τ > 18 mins, catalyst activity at s = 0.8 was lower than at s = 0.5 because of the longer time spent in the propane-rich region of the cycle and the relatively slower rate of carbon removal resulting in a reduced time-average product formation. While both H₂ and CO rates were enhanced with periodic operation, Fig. 3 shows that the selectivity ratio decreased from about 3 passing through a minimum at τ = 12 mins before an upturn beyond τ = 15 mins. However, the H₂:CO ratio was always lower than the steady-state value. This suggests that periodic operation can be used to tune product selectivity to desired values depending on the downstream requirement of the synthesis gas. For example, optimum syngas composition for Fischer-Tropsch reaction for GTL production is about H₂:CO = 2 while a much higher ratio is needed for ammonia synthesis. The flexibility introduced by periodic composition forcing is advantageous if the syngas production plant is expected to meet the specifications for different customer needs.

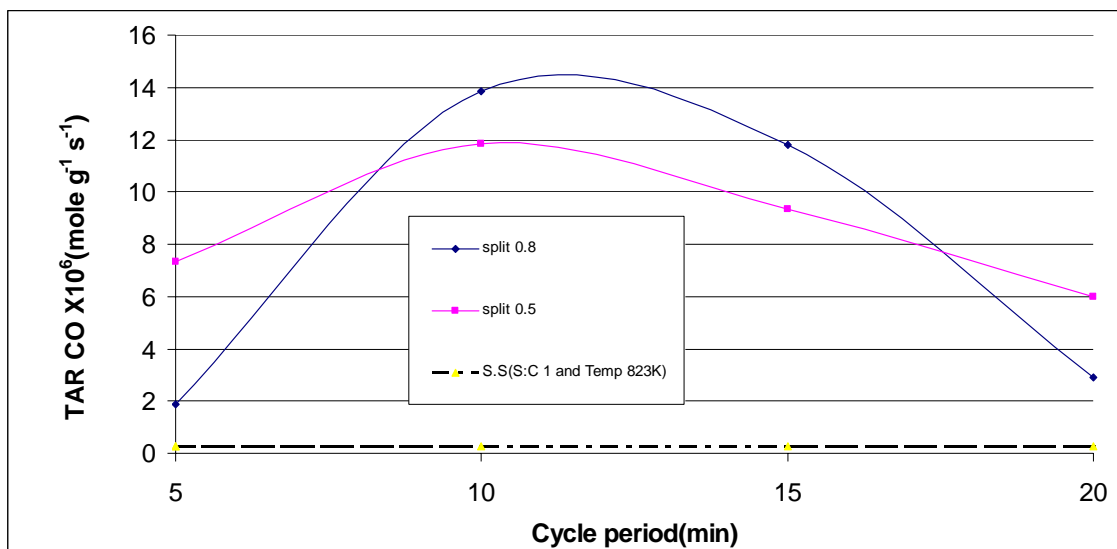


Fig 2: Effect of cycle period and split on CO formation

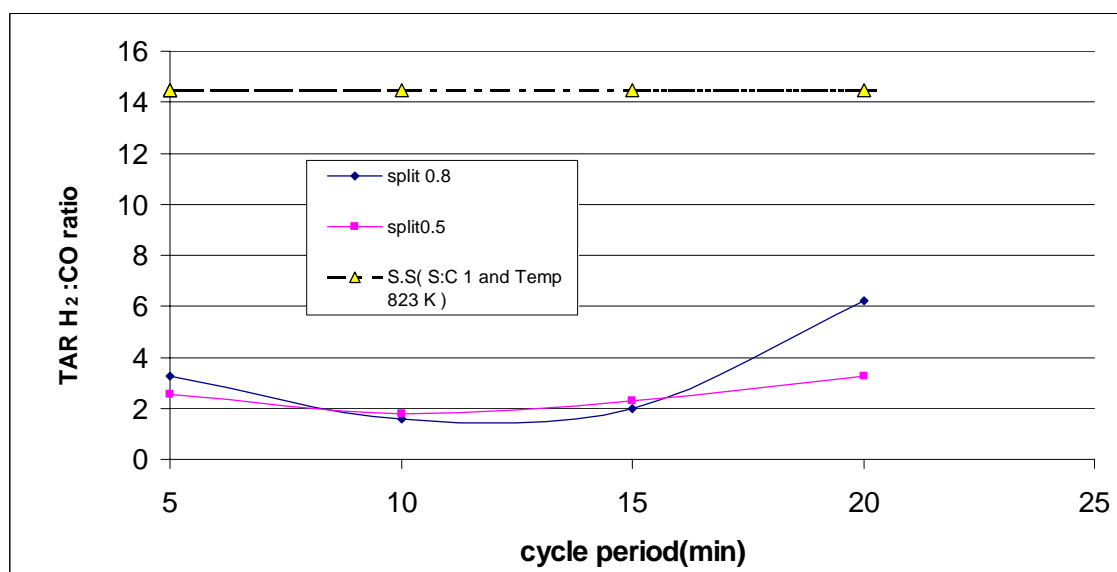


Fig 3: Effect of cycle period on H₂:CO ratio

CONCLUSIONS

This study which is part of a larger program on enhanced operation of coke-induced deactivated reactors through periodic control suggests that composition forcing between feed containing low steam-to-carbon ratio and CO₂ can lead to significant improvements (2 to 5-fold) in both H₂ and CO formation rates with reduced (or practically nil) carbon deposition on the catalyst.

The associated minimal changes in the structural attributes of the catalyst suggest that catalyst longevity and stability may be substantially extended without the added down-

time in conventional regenerators. Additionally, the potential for using lower steam:carbon ratio feed than current practice (>3) will lead to reduction in energy costs (due to reduced steam demands) and better utilisation of effluent CO_2 (a GHG) from the petrochemical industries. Periodic composition forcing has also opened opportunities for tuning product selectivity ($\text{H}_2:\text{CO}$ ratio) to specific customer needs without extensive plant reconfiguration.

As a pioneering study, future plans include detailed analysis of the reaction dynamics under composition cycling and identification of possible resonant effects.

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