

# RESONANCE EFFECTS IN PRODUCT FORMATION RATE DURING PERIODIC COMPOSITION CYCLING BETWEEN PROPANE STEAM REFORMING MIXTURE AND CARBON DIOXIDE

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## Summary

This paper reports the occurrence of multiple maxima in the time-average product formation rate with cycle frequency (0.2 to 10 mHz) when the feed to the fluidized bed reactor was alternatively switched between the reactants for propane steam reforming (steam:carbon ratio =1) and CO<sub>2</sub> (which was used as a carbon gasifying agent). Resonant behaviour was also a function of the cycle split (0.1 to 0.9) employed. Product rates under periodic operation were 4 to 40-times higher than the equivalent steady-state rate. However, the time-average H<sub>2</sub>:CO product ratio dropped rapidly from 9 at 0.28 mHz to nearly constant value (1.4) for cycle frequency between 0.83 to 8.3 mHz. The ability to tune activity and product selectivity simultaneously may be attributed to a synergistic confluence of different surface reaction dynamics for coke gasification and propane dehydrogenation and the concentration wave transport.

## Keywords

Periodic operation, steam reforming, hydrogen production, catalyst regeneration synthesis (e) reduction in reformer shutdown for catalyst revivification.

## Introduction

Reaction behaviour under forced composition modulation has been the subject of extensive experimental and theoretical studies<sup>1-2</sup>. In a recent publication<sup>3</sup>, we have compared several carbon gasifiers and demonstrated that CO<sub>2</sub> is a more effective coke gasification agent than oxygen since it does not lead to catalyst sintering or other detrimental structural effects. The control of catalyst deactivation via periodic composition cycling with a gasifying agent such as CO<sub>2</sub> has not been previously examined but has several interesting advantages, namely; (a) in-plant utilization of CO<sub>2</sub> (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 H<sub>2</sub> and CO formation rates since both are generated during each section of the cycle albeit via different routes (d) flexibility in H<sub>2</sub>:CO ratio permitting tunability to meet different downstream requirements e.g. in GTL fuels

## Experimental

Steam reforming runs were carried out over reduced Co-Ni/Al<sub>2</sub>O<sub>3</sub> catalyst as described in our previous paper<sup>3</sup>. Cycle period,  $\tau$ , was varied between 2 to 60 minutes at different cycle split,  $s$  (0.1, 0.3, 0.5, 0.7 and 0.9) using electrically actuated solenoid valves. BET surface area for both fresh and regenerated catalysts was collected at 77 K on a Quantachrome Autosorb-1 unit. The organic carbon content in the coked and regenerated catalysts was also obtained from a Shimadzu Total Organic Carbon Analyzer (model SSM-5000). CO<sub>2</sub> and NH<sub>3</sub> temperature-programmed desorption (TPD) were performed on a Micromeritics AutoChem 2910 at 973 K while H<sub>2</sub> chemisorption was conducted in the same apparatus at 383 K.

## Results and Discussion

Fig.1 illustrates the influence of cycle split on time-average rate (TAR) for H<sub>2</sub> for cycle period

between 10-60 minutes. The appearance of a maximum peak for all splits examined suggests that H<sub>2</sub> was produced relatively rapidly in both sections of the cycle period via:  $C_3H_8 \rightarrow (2/x)C_xH_{1-x} + CH_4 + [(3x-1)/x]H_2$  and  $C_xH_{1-x} + xH_2O \rightarrow xCO + [(x+1)/2]H_2$  in the steam reforming partial cycle while coke removal may be effected through  $C_xH_{1-x} + xCO_2 \rightarrow 2xCO + [(1-x)/2]H_2$  and  $C_xH_{1-x} + [(5x-1)/4]CO_2 \rightarrow [(5x-1)/2]CO + [(1-x)/4]CH_4$  in the CO<sub>2</sub>-rich section of the cycle. It is apparent that the time-average product (H<sub>2</sub>, CO and CH<sub>4</sub>) formation rate would exceed that for steady-state operation since coke is consumed over the entire cycle period.

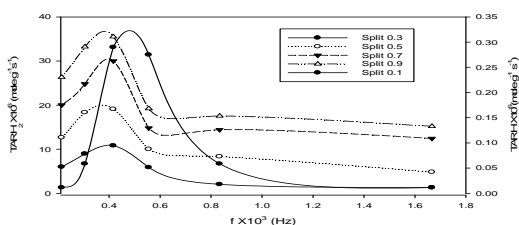


Fig. 1: Effect of cycle split on time-average rate for H<sub>2</sub> at 873 K using S:C = 1.

However, a constructive interaction between surface relaxation time constants for these species and concentration wave velocity through the carbonaceous deposit would account for the existence of troughs and crests in the TAR-cycle frequency profile even if linear surface reaction kinetics is assumed. However, the optimal cycle frequency shifted to lower value with decreasing cycle split. As Fig. 2 shows, for symmetrical composition wave, resonant peaks may be obtained under both fast and slow cycling implicating the nonlinear character of the reaction kinetics. Additionally, the product H<sub>2</sub>:CO ratio dropped sharply at low frequency to 1.4 and remained constant thereafter. Interestingly, this value is below that for steady-state operation due to effective utilization of the CO<sub>2</sub> for coke removal. Thus, the product stream may be used as feed for a Fischer-Tropsch reactor. The practical benefits of this mode of reactor operation lie not only in activity and product selectivity enhancement but also increased catalyst longevity and stability due to substantial reduction in coke deposition with time-on-stream. Although not shown, analyses of the total organic carbon content in used catalyst specimens from various runs complement the

product TAR trends. A discussion of plausible mechanistic basis for the experimental data is given in the full length paper.

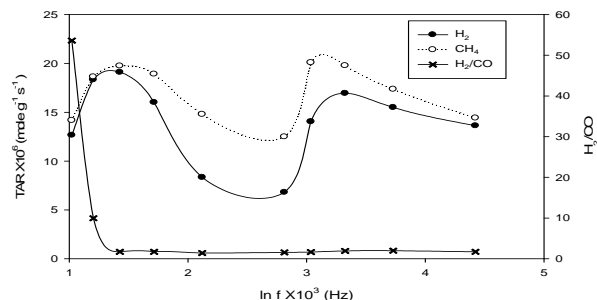


Fig. 2: Effect of cycle frequency on H<sub>2</sub>:CO product ratio at 873 K using S:C = 1 for cycle split, s = 0.5.

## Conclusions

This investigation reports the benefits of periodic composition cycling of hydrocarbon steam reforming reaction with a suitable carbon gasifying agent in terms of improved catalyst activity and stability. In particular, we demonstrated that both cycle period and symmetry have strong influence on reactor performance.

## References

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