BIOREACTOR SCALE-UP FOR WATER-GAS SHIFT REACTION

G. D. Najafpour, R. Basu, E. C. Clausen and J. L. Gaddy

Deparment of Chemical Engineering
University of Arkansas
Fayetteville, AR 72701, USA

Abstract A scale-up study has been performed with three different size reactors to establish the optimum operating conditions for the hydrogen production from synthesis gas by biological water-gas shift reaction using the photosynthetic bacterium *Rhodosprillium rubrum*. Optimum medium composition and operating conditions previously determined in a bench scale 1.25 L continuous stirred tank reactor (CSTR) were used for this study with geometrically similar 2.5, 5.0 and 14.0 L CSTR. The hydrogen production rate, cell concentration and carbon monoxide (CO) conversion were monitored in this scale-up study. The light energy supply was linearly increased with the working volume of the reactors. The agitation rates were determined by the equal power/volume rule. There were good agreement between the calculated agitation rates and the experimentally observed values for all the three different reactors. A 70% carbon monoxide conversion was obtained with 30, 60 and 150 sccm gas flow rate for the 2.5, 5.0 and 14.0 L fermentors respectively. At 70% CO conversion the 2.5 and 5.0 L reactors showed 25% improvement in performance and the 14.0 L reactor showed 11% improvement. The estimated mass transfer coefficients for all four reactors showed very similar values under the optimum operating condition (average K_La= 117 h-1). A 664 h long performance of the process show very stable behavior.

Key Words Bioreactor Scale-up, Water-gas Shift, Hydrogen Production, *Rhodospirillum Rubrum*, Photosynthetic Bacterium

چکیده مطالعاتی درباره کاربرد بیوراکتورها در شرایط عملیاتی بهینه جهت تولید هیدروژن از گاز سنتز در واکنش جابجایی آب-گاز با استفاده از باکتریهای فتوسنتز Rhodosprillium rubrum انجام شد. ترکیب محیط کشت بهینه شده و شرایط بهینه کارکرد ارگانیزم نیز قبلاً در بیورکتور ۱/۲۵ لیتری تعیین گردید. با بکارگیری تشابه هندسی بیوراکتورهای ۲/۵، ۵ و ۱۴ لیتری از نوع CSTR میزان تولید هیدروژن، غلظت یاخته و درصد تبدیل گاز منوکسید کربن مورد مطالعه و کنترل دقیق قرار گرفت. میزان انرژی نوری جهت رشد ارگانیزم با افزایش مقیاس بیوراکتورها دارای رابطه ای خطی است. سرعت همزن از قانون تساوی توان به حجم بیوراکتور پیروی نموده و سرعت محاسبه شده همزن با سرعت تجربی در سه بیوراکتور با اندازه های مختلف تطابق بسیار خوبی با یکدیگر داشتند. میزان تبدیل CO در بیوراکتور کوچک ۷۰ درصد بود که در بیوراکتورهای ۲/۵ و ۵ لیتری ۲۵٪ افزایش یافت. این افزایش در بیوراکتور ۱۴ لیتری به ۱۱٪ رسید. ضریب انتقال جرم در چهار بیوراکتور درتحت شرایط عملیاتی بهینه نزدیک به یکدیگر و درحدود K_La= ۱۱۷h^{-1} تخمین زده شد. طولانی ترین زمان عملیاتی ۶۶۴ ساعت و در بیوراکتور ۱۴ لیتری بود که درطی این مدت بیوراکتور از پایداری مناسبی برخوردار بود.

INTRODUCTION

Biomass has the potential to be converted to synthesis gas [1,2] (principally H_2, CO_2 and CO) which in turn can be converted to liquid fuels. Synthesis gas needs to have an H_2: CO ratio of at least 2:1 to produce liquid fuels [3].

$$CO + 2H_2 \rightarrow CH_3OH \quad (1)$$

$$2CO + 4H_2 \rightarrow C_2H_5OH + H_2O \quad (2)$$

The hydrogen content of the synthesis gas can be increased by employing the water-gas shift reaction [4]:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (3)$$

In order to improve the H_2 content of the synthesis

gas, the biological route has been considered. Biological water-gas shift reaction may be an alternative to catalytic processes for the conversion on biomass to fuels and chemicals [3,5,6].

The purple non-sulfur bacterium *Rhodospirillum rubrum* [7] has been used for the production of hydrogen from syngas [5,6]. It has been observed that *Rhodospirillium rubrum* can convert carbon monoxide in light or darkness, but light is essential for growth [5]. It should be noted that carbon monoxide is not the limiting carbon source for growth. Instead, growth occurs on yeast extract and other organic carbon sources (e.g. sodium acetate) present in the medium. The optimum operating conditions for this biochemical process of hydrogen production has been discussed elsewhere [3].

A scale-up of the process is necessary to evaluate the economic feasibility of the process against the conventional process. Most scale-up in industrial practice are conducted by keeping selected parameters constant with change in scale [8]. The most common parameters used are: (1) equal power / volume ratio; (2) equal K_La; (3) equal shear; (4) equal mixing; (5) combination of K_La, shear and mixing. Most methods assume geometric similarity, though in practice minor adjustments are made to keep all relevent parameters within desired ranges.

The method of equal/volume ratio has been used for this fermentation system as a primary scale-up parameter. It is known that power/volume requirements decrease with an increase in scale.

The objective of this scale-up study in the stirred tank fermentors is to verify the conditions for bacterial cell growth and the desired level of CO conversion to produce hydrogen developed in a 1.25 L bench-scale fermentor. The mass transfer coefficients were estimated [9] for each reactor under the condition of ~70% CO conversion.

MATERIALS AND METHODS

Rhodospirillum rubrum [7], ATCC 25903, was obtained from American Type Culture Collection (Rockville, MD). It was grown on a basal medium containing: yeast extract (Difco) 0.5 g, Pfennig's minerals solution [10], 50 mL; Pfennig's trace metal solution [11], 1 mL; B-vitamins solution; 5 mL; ammonium chloride, 3 g; sodium acetate, $3H_2O$, 6 g; and sodium bicarbonate, 3 g, in one liter of medium. The liquied medium was autoclaved at 121°C and 2 atm pressure.

The continuous stirred tank reactors (CSTR) used for the experiments were two New Brunswick Scientific (Edison, NJ) BioFlo IIc fermentors equipped with temperature, pH and agitation control and a Virtis model 43-100 fermentor (Virtis Co, Gardiner, NY). The agitation system in the reactors has two disk type turbine impellers. The liquid working volumes in the reactors were 2.5, 5.0 and 14.0 L, respectively, and the overhead gas volumes were 0.8, 1.6 and 6.0 L, respectively. Illumination necessary for growth was supplied by two tungsten lights (60 w lamps for BioFlo reactors and 100 w lamps for virtis fermentor). The incident light intensities on the outer wall of the reactors were measured with an LX-101 digital lux meter (Cole-parmer, Chicago, IL). The incident light intensity from each lamp were 2500, 5000 and 9000 lux for the three reactors, respectively. Experiments were carried out at pH 7 and at a temperature of 32°C. The feed gas was a mixture of H_2, Ar, CO, CO_2 (20/15/55/10% v/v) and was continuously fed to the reactors. Liquied medium was also supplied on a continuous basis.

Typically experiments were started with constant agitation rate, gas flow rate, light illumination and liquid flow rate. The cell concentration, hydrogen production and percentage of carbon monoxide conversion were monitored and several data were col-

lected to establish steady state condition.

Experiments were performed to establish the scale-up procedure at optimum operating conditions for cell growth, percent carbon monoxide conversion and hydrogen production obtained from the 1.25 L reactor. Light illumination was increased linearly with the liquid working volume of the reactors. Agitation rate was determined by the equal power/volume rule [8, 12-14]. Once each reactor was operated under the optimum condition determined previously, experiments were performed condition determined previously, experiments were performed to investigate carbon monoxide conversion and hydrogen production at different gas flow rates under the operating condition. A time duration study was also performed to show the stability of the 2.5 L and 14.0 L reactors at optimum operating condition.

A concentrated medium (seven times concentrated) along with sterile deionized water used for the 14.0 L Virtis fermentor (Figure 1). The filtered water was used to maintain the liquid dilution rate. A sterile filter with a porosity of 0.2 μm (Gelman. Ann arbor, Michigan) was used for the filtration of deionized water. Prior to filtration, the water was purged with helium for 4 hours in order to take out any dissolved gas.

The dry cell weight concentrations (mg/L) were determined by measuring optical density at 540 nm in a Spectronic 21 spectrophotometer (Milton Roy Co, Rochester, NY) and converted to dry weight cell concentration using a calibration curve.

Gas compositions were measured by a gas chromatograph (Sigma 300, Perkin Elmer, Norwalk, CT) with a 1.8 m × 3 mm carbosphere (Alltech, Deerfield, IL) 60/80 mesh column. The carrier gas was helium with a flow rate of 40 mL/min. The oven temperature was maintained at 100°C, while injector and thermal conductivity detector temperatures were 170°C. Acetate in the liquid phase was measured by a gas chromatograph (HP 5890 series II with HP chemstation data processing software, Hewlett-Parckard, Avondale, PA) with a 1.5 m× 3 mm column packed with porapak QS (Alltech), 100/120 mesh column. The carrier gas was nitrogen at a flow rate of 55 mL/min. The oven tem perature was maintained at 190°C, while the injector and flame ionization detector temperatures were 240 °C. 1-propanol was used as the internal standard for acetate analysis.

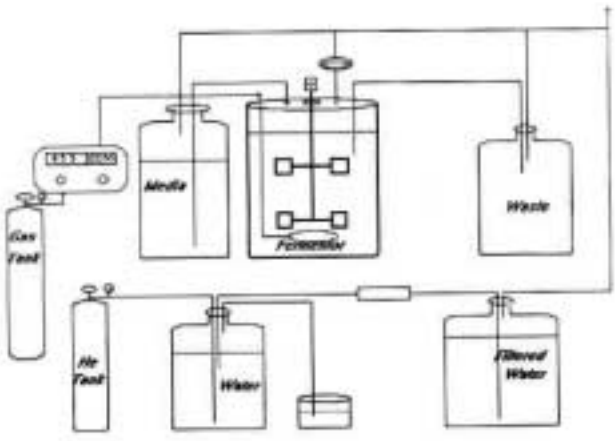

Figure 1. The Schematic diagram of the 14 L fermentor.

RESULTS AND DISCUSSION

The equal power per unit volume rule was applied for the scale-up of geometrically similar in the continuous stirred tank reactors (CSTR) for hydrogen production using *R. rubrum*. Table 1 presents the geometric dimensions of the reactors used for this scale-up study. In the first stage of the scale-up study, a 2.5 L CSTR was used. The operating conditions were chosen based on the performance of a 1.25 L CSTR [3]. The liquid dilution rate was chosen by keeping the liquid retention time constant. The light requirement was in the range of 500-1100 lux for the 1.25 L reactor; therefore, 2500 lux light energy was sufficient for the 2.5 L reactor. Since the liquid working volume was doubled, it was expected that the gas

TABLE I. Geometric Dimensions of Fermentors.

V_L (L)	V_G (L)	D_t (cm)	D_i (cm)	D_i/D_t	H_L/D_t	H_t/D_i	H_b/D_i	H_{i-i}/D_i	N_i
1.25	0.35	12.0	5.40	0.45	1.12	0.76	0.53	1.20	2
2.5	0.80	13.3	6.50	0.49	1.43	1.07	0.53	1.27	2
5.0	1.60	17.1	7.78	0.45	1.40	1.07	0.49	1.59	2
14.0	6.00	24.8	11.4	0.46	1.10	0.84	0.44	1.12	2

flow rate may also be doubled for the same level of CO conversion. However the gas flow rate was increased by 25% for the same level of CO conversion in the 2.5 L CSTR. Figure 2 shows the gas flow rate variation studies in this reactor. At a gas flow rate of 30 sccm (83.33 min gas RT) a 70% CO conversion was obtained. As the gas flow rate was increased to 89 sccm (28.1 min gas RT) CO conversion dropped to 24%. Hydrogen production increases linearly at low gas flow rate. At higher gas flow rates, hydrogen production rate remained constant. Also, fluctuation of hydrogen production has been observed at 74 sccm (33.78 min gas RT) gas flow rate.

Figure 3 presents the data for the liquid dilution rate variation study with 2.5 L reactor. A 40% improvement in CO conversion was observed as the liquid dilution rate was tripled. However, the cell concentration was gradually decreased. The liquid dilution rate was varied in order to show the effect of liquid dilution rate on CO conversion. The hydrogen production rate was stable as the liquid dilution rate was varied. The CO conversion was 50% at the liquid dilution rate of 0.21 day^{-1}. As the liquid dilution rate was increased to 0.67 day^{-1} the CO conversion improved to 70%.

Figure 4 presents the agitation rate variation study with the 2.5 L reactor. The hydrogen production rate was low at low agitation rate. As the agitation rate was increased to 540 rpm or above, the CO conversion reached 70% and the hydrogen production rate was also improved. At high agitation rates, the CO conversion and hydrogen production rate remained constant. The cell concentration fluctuated during agitation rate variation studies (the average cell con-

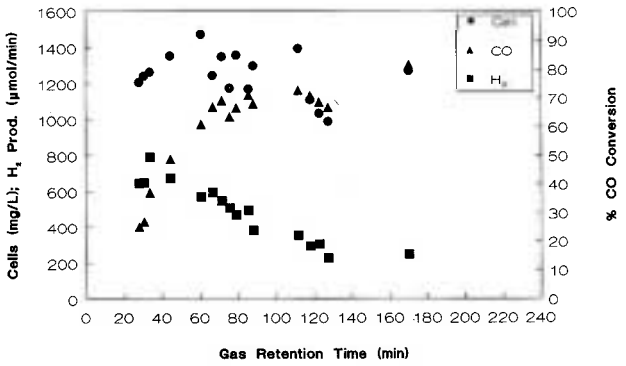

Figure 2. The Effect of gas retention time on cell concentration, CO conversion and H_2 production using *R. rubrum* in the 2.5 L CSTR.

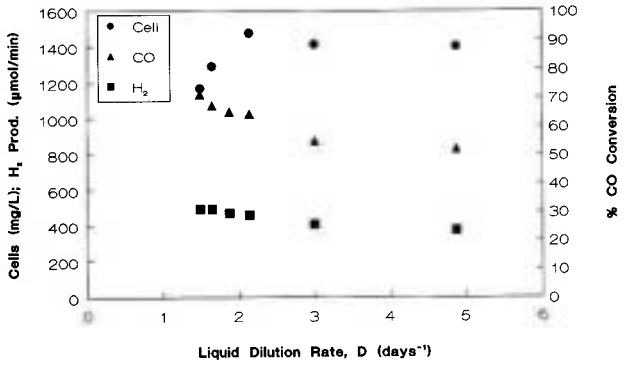

Figure 3. The Effect of liquid dilution rate on cell concentration, CO conversion and H_2 production using *R. rubrum* in the 2.5 L CSTR.

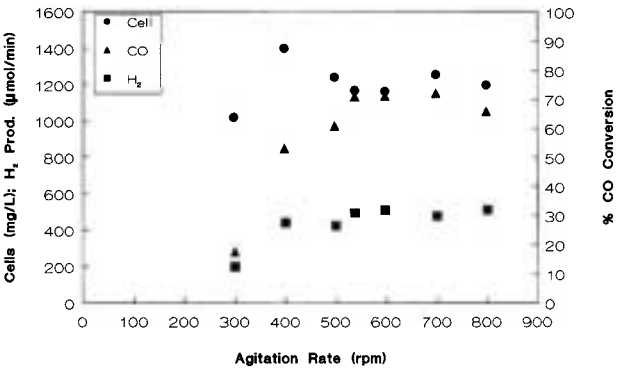

Figure 4. The effect of agitation rate on cell concentration, CO conversion and H_2 production using *R. rubrum* in the 2.5 L CSTR.

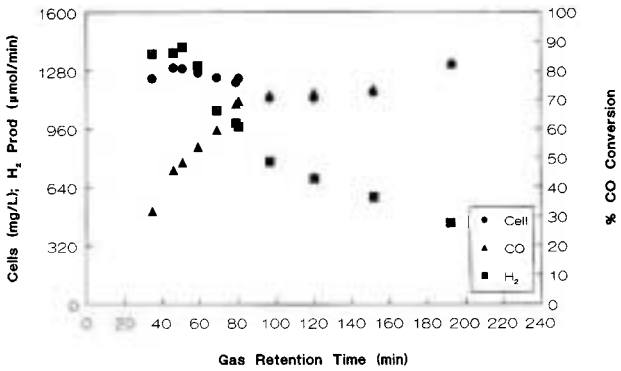

Figure 6. The effect of gas retention time on cell concentration, CO conversion and H_2 production using *R. rubrum* in the 5.0 L CSTR.

centration was about 1200 mg/L). The optimum agitation rate was compatible with the value obtained by the rule of constant power per unit volume. The optimum agitation rate for the 2.5 L fermentor was 540 rpm. It was the same as the calculated agitation rate based on constant power required per unit volume.

Figure 5, shows the stability of the 2.5 L fermentor for 664 hours of operation, running at optimum operating conditions. The CO conversion was practically constant at 70%. There were small fluctuations on hydrogen production rate and cell concentration. The average cell concentration was 1250 mg/L. The average hydrogen production rate was 425 µ mol. min^{-1}.

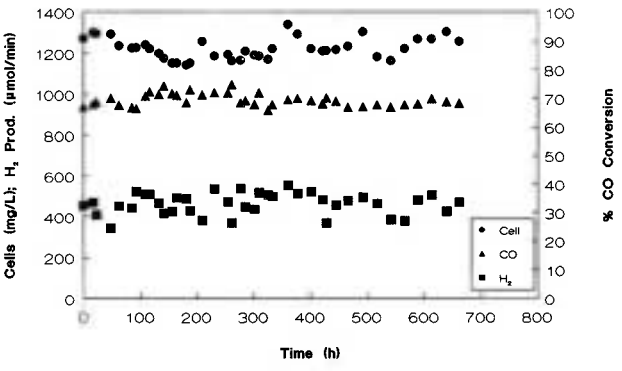

Figure 5. The stability of 2.5 L CSTR for cell concentration, CO conversion and H_2 production using *R. rubrum*.

The optimum operating conditions of 1.25 L reactor also utilized to scale up the 5.0 L CSTR. The effects of gas flow rate and agitation rate were studied in this reactor. Figure 6 shows the gas flow rate variation between 25 and 140 sccm (200 and 35.7 min gas RT). As the gas flow rate was increased, the CO conversion was linearly decreased and the hydrogen production rate was increased. The cell concentration was constant, except in the beginning when there was mechanical problem with the nutrient pump. There was a small drop in cell concentration during that period. The average cell concentration was 1280 mg/L. The optimum gas flow rate for 70% CO conversion was 60 sccm (83.33 min gas RT) for the 5.0 L CSTR. Comparison of 2.5 L and 5.0 L fermentors shows that the gas flow rate can be doubled as the working volume is doubled for the same level of CO conversion.

Figure 7 represents the agitation rate varied from 300 to 800 rpm, while other parameters were fixed. Based on equal power per unit volume rule, the calculated agitation rate for the 5.0 L reactor is 490 rpm. The calculated agitation rate was compatible with that experimental data. The CO conversion and hydrogen production were improved as the agitation rate was increased. At high agitation rate, the CO conversion and hydrogen production rates were con-

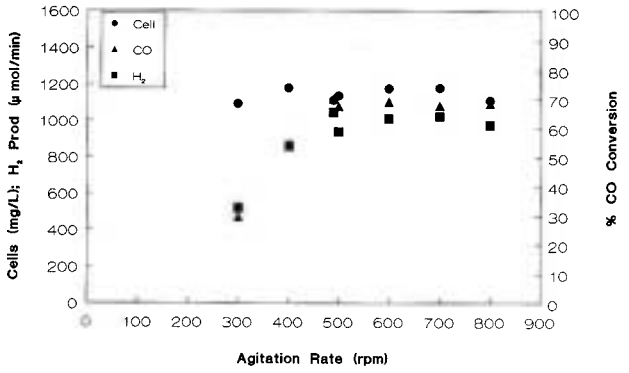

Figure 7. The effect of agitation rate on cell concentration, conversion and H_2 production using *R. rubrum* in the 5.0 L CSTR.

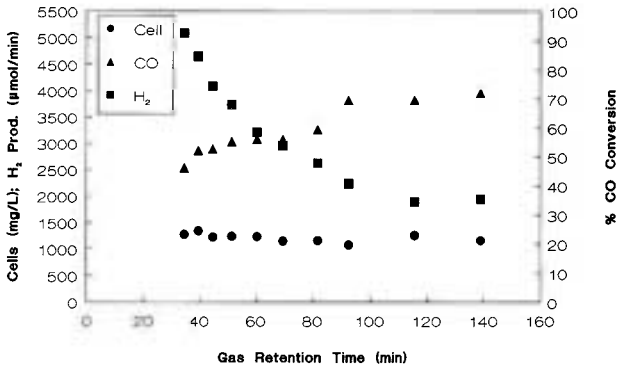

Figure 8. The effect of gas retention time on cell concentration, CO conversion and H_2 production using *R. rubrum* in the 14.0 L CSTR.

stant. The cell concentration was in a constant level during this set of experiments. The hydrogen production rate was 1000 μ mol. min^{-1} with a gas flow rate of 60 sccm, agitation rate of 490 rpm, and CO conversion of 70%.

Figure 8 shows the gas flow rate variation studies in a 14 L CSTR fermentor. As the gas flow rate increased the CO conversion was gradually decreased. The cell concentration was quite stable at 1200 mg/L. The hydrogen production rate was linearly increased as the gas flow rate was increased. The CO conversion dropped to 46% at the gas flow rate of 402 sccm (34.83 min gas RT). A 70% CO conversion was obtained with 150 sccm of gas flow rate (93.33 min gas RT). The hydrogen production rate was increased to 5100 μ mol. min^{-1} as the gas flow rate was increased to 402 sccm (34.83 min gas RT). The agitation rate was also calculated based on equal power per unit volume rule. A constant agitation rate of 400 rpm was used for the 14 L CSTR.

Figure 9 shows the stability of the 14.0 L fermentor for 440 hours of operation, running at optimum operating condition. The nutrient used was a seven times concentrated media and deionized filtered water for liquid dilution and cells wash out purposes. After 140 hours of operation, the reactor was toxicated; therefore, the CO conversion, cell concentration and hydrogen production rates were gradually dropped. The reactor was restored by replacing regular media and the operation was continued for another 150 hours. A five times concentrated media was replaced with deionized and filtered water for 150 hours of operation. The CO conversion was maintained above the 70% with the gas flow rate of 150 sccm, concentrated media flow rate of 1400 mL day^{-1} and water flow rate of 8160 mL day^{-1}. The total liquid dilution rate was 0.68 day^{-1}. The hydrogen production rate was 2500 μ mol. min^{-1} during the experiment.

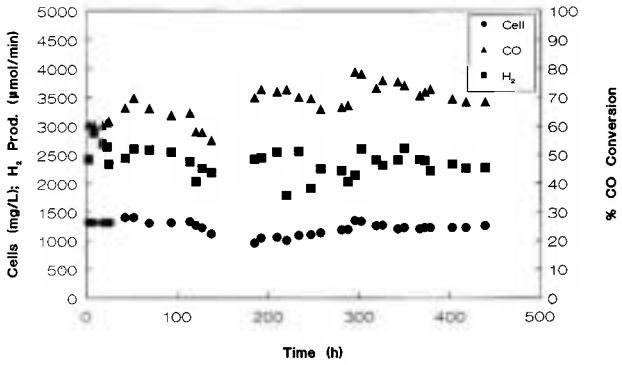

Figure 9. The stability of 14.0 L CSTR for cell concentration, CO conversion and H_2 production using *R. rubrum*.

TABLE II. Mass Transfer Coefficients for Different Agitation Rate.

Agitation Rare, rpm	Gas Flow Rate, sccm	%CO Conversion	H_2/CO	K_La, h^{-1}
1.25 L Reactor				
200	7.035	20.56	0.70	5.30
300	7.035	26.55	0.90	7.80
400	7.035	39.96	1.20	14.64
500	7.035	60.00	2.375	33.16
600	7.035	81.35	5.37	106.00
700	7.035	72.55	3.53	63.71
800	7.035	65.75	2.60	44.00
2.5 L Reactor				
300	29.00	17.65	0.79	9.40
400	29.65	53.20	2.09	56.74
500	29.57	60.94	2.45	78.20
540	29.03	71.10	3.70	122.82
600	29.00	71.26	3.78	125.10
700	29.24	72.23	3.74	130.32
800	32.05	65.91	2.99	107.34
5.0 L Reactor				
300	61.95	29.43	1.01	19.65
400	61.71	54.37	2.05	60.79
490	59.13	70.24	3.68	121.24
500	60.79	67.58	3.10	107.29
600	60.33	69.21	3.44	117.98
700	60.69	67.79	3.30	110.63
800	60.89	68.53	3.25	115.72
14.0 L Reactor				
400	150.75	72.02	3.15	116.43

The mass transfer coefficients were constant for the scale up study. They were 106.0, 121.24, 122.82 and 116.43 h^{-1} for the 1.25, 2.5, 5.0 and 14.0 L reactors, respectively. The masstransfer coefficient obtained from the 14.0 L reactor was averaged with constant gas retention time of 93.3 min. Table 2 represents the mass transfer coefficients obtained with different agitation rates. At a low agitation rate, the reactors were less productive; therefore, low mass transfer coefficients were shown. The maximum productivity was obtained at the desired condition with high mass transfer coefficient. The constant mass transfer coefficient for the scale up purpose in the above reactors were at 120 h^{-1}.

CONCLUSIONS

The operating conditions media composition developed in a bench scale study has been utilized for a bioreactor scale-up study for water-gas shift reaction with photosynthetic bacterium *R. rubrum*. A steady state approach was employed to obtain stable condition. Maximum hydrogen production with CO conversion of 70% at gas flow rate of 30, 60 and 150 sccm were obtained in 2.5, 5.0 and 14.0 L reactors. High gas flow rates yielded high hydrogen production rates as CO conversion was gradu-

ally dropping.

ACKNOWLEDGEMENT

The work presented in this paper was made possible through the financial support of the U.S. Department of Energy, Morgantown Energy Technology Center, under grant number DE-FG21-90MC27225.

NOMENCLATURE

D	diameter, cm
H	height, cm
N	number
V	volume, L

Subscripts

b	bottom
G	gas
i	impller
L	liquid
t	tank

REFERENCES

1. W. Black, K.G. Bircher and K. A. Chisholm, "Fluidized-bed Gasification of Solid Wastes and Biomass: the CIL Program," (1980) 351-361, In: J. L. Jones and S. B. Radding (ed.), Thermal Conversion of Solid Wastes and Biomass, Acs Symposium Series 130, American Chemical Society: Washington, DC.
2. S. A. Vigil, D. A. Bartley, R. Healy and G. Tchobanoglous, "Operation of a Downdraft Gasifier Fueled with Source-Separated Solid Waste," (1980) 257-274, In: J. L. Jones and S. B. Radding (ed.), Thermal Conversion of Solid Wastes and Biomass, ACS Symposium Series 130, American Chemical Society: Washington Dc.
3. D. G. Najafpour, R. Basu, E. C. Clausen and J. L. Gaddy, "Water-Gas Shift Reaction for Synthesis Gas: A Biological Route," Submitted for publication, *J. Energy & Fuels* (1993).
4. Kirk-Othmer, "Fuels, Synthetic. Encyclopedia of Chemical Technology", 3rd edition, vol. 11. John Wiley, New York. (1982) 410-412.
5. J. P. Cowger, K. T. Klasson, M. D. Ackerson, E. C. Clausen and J. L. Gaddy, "Mass-transfer and Kinetic Aspects in Continuous Bioreactors Using Rhodospirillum rubrum," *Appl. Biochem. Biotechnol.* 34/35, (1992), 613-624.
6. K. T. Klasson, A. Gupta, E. C. Clausen and J. L. Gaddy, "Evaluation of Mass Transfer and Kinetic Parameters for *Rhodospirillum rubrum* in a Continuous Stirred-Tank Reactor," *Appl. Biochem. Biotechnol.* 39/40, (1993), 549-557.
7. J. T. Staley (ed.), "Bergey's Manual of Systematic Bacteriology". Baltimore, MD. USA Williams & Wilkins, Vol. 3, (1989) 1664-1665.
8. V. Singh, R. Fuchs and A. Constantinides, "A New Method for Fermentor Scale-up Incorporating both Mixing and Mass Transfer Effects-I. Theoretical Basis. (1987) 200-214. In: C. S. Ho and J. Y. Oldshue (ed.), Scale-up and Mixing. AICHE, New York.
9. K. T. Klasson, K. M. O. Lundback, E. C. Clausen and J. L. Gaddy, Kinetic of Light Limited Growth and Biological Hydrogen Production from CO and H_2O by *R. rubrum*". *J. Biotechnol.* 29, (1993), 177-188.
10. M. J. McInerney, M. P. Bryant and N. Pfenning, "Anaerobic Bacterium that Degrades Fatty Acids in Syntropic Association with Methanogens". Arch. Microbiol. 122, (1979), 129-135.
11. B. R. S. Genthner, M. P. Davis and M. P. Bryant, "Features of Rumen and Sewages Sludge Strains of Eubacterium Limosum, a Methanol- and H_2–CO_2 - Utilitizing Species", *Appl. Environ. Microbiol.* 42, (1981), 12-19.

12. S. Aiba and A. E. Humphrey, N. F. Millis, "Biochemical Engineering,"Chap. 7, 2nd Edition, Academic Press, Inc., New York (1973).
13. J. E. Baily and D. F. Ollis, "Biochemical Engineering Fundamentals," 2nd Edition, McGraw-Hill, New York (1986).
14. D. W. Hubbard, "Scale-up Strategies for Bioreactors (1987), 168-184. In: Scale-up and Mixing; C. S. Ho, J. Y. Oldshue (ed.), AICHE, New York.