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AN ANALYSIS OF WATER GAS-SHIFT REACTOR BATTERY SYSTEM FOR SYNTHESIS GAS REFINEMENT

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ABSTRACT

In this study, a two-stage synthesis gas (SYNGAS) refinement process is modeled through the use of a water-gas-shift (WGS) reactor battery system. The process is controlled by adjusting the mixing ratio via a bypass line between the inlet and exit streams of the WGS reactor battery system, and the amount of steam supply into each reactor. Steam requirements and the amount of synthesis gas passing through the bypass line are determined by satisfying the constraints of the ratio of hydrogen to carbon monoxide at the exit of the system. The characteristic behavior of the battery system is obtained depending on the synthesis gas composition. As a result, the structured model cannot only refine the synthesis gas composition, but also identify the proper process parameters for a given coal type.

Keywords: Water Gas-Shift reactor battery, synthesis gas refinement, two-stage process

SENTEZ GAZI İYİLEŞTİRMESİ İÇİN SU GAZI DÖNÜŞÜM REAKTÖR BATARYA SİSTEMİNİN ANALİZİ

ÖZET

Bu çalışmada, iki kademeli sentez gazı iyileştirme prosesi, Su Gazı Dönüşüm (SGD) reaktör batarya sistemi kullanılarak modellenmiştir. SGD reaktör batarya sisteminin giriş ve çıkış akımları arasında bypass hattı ile karışım oranı ve her reaktöre gönderilen buharın miktarı ayarlanarak proses kontrol edilmiştir. Buhar gereksinimi ve bypass hattından geçen sentez gazı dönüşüm miktarı, sistem çıkışındaki hidrojen-karbon monoksit oranı sınırlamaları dikkate alınarak belirlenmiştir. Batarya sisteminin karakteristik davranışı, sentez gazı kompozisyonuna bağlı olarak elde edilmiştir. Sonuç olarak, yapısal model, sentez gazı kompozisyonunu iyileştirebilmesinin yanında, aynı zamanda, verilen bir kömür tipi için uygun proses parametrelerini tanımlayabilmektedir.

Anahtar kelimeler: Su Gazı Dönüşüm reaktör bataryası, sentez gazı iyileştirme, iki-kademeli proses

1. INTRODUCTION

Increasing energy demand has enormously forced human-being to develop new energy efficient technologies for the last century. Nevertheless, environmental factors have seemed to be forgotten during this period. Care should be taken of the protection of our environment from hazardous effects of bulk energy production by introducing new applicable methods. In this respect, integrated gasification combined cycle (IGCC) for power generation is one of the prominent alternatives. Besides, it should not be forgotten that the power generation systems based on gasification have always higher overall efficiency as compared to the conventional systems. Therefore, it seems that more attention would be payed to the production of syngas for power generation in the future. For all that, the application of gasification technology to power generation needs to be improved.

There are numeruous contemporary studies related to the syngas production for power generation in the literature. A review of the basic technology of coal gasification, with particular application to the production of syngas for power generation is presented in the study of Casleton et.al. [1]. There are usefull and considerably large amount of references in the study.

This study is focused on the determination of the range of operating conditions for the refinement of syngas from coal aimed to use in power generation. Optimization study is performed for obtaining the most proper process parameters.

2. DESCRIPTION OF THE SYSTEM

Achieving the best SYNGAS composition for power generation and production of coal chemicals is a challenging problem. There are many parameters effecting the composition of syngas which makes the problem more complex.

A two-stage WGS reactor is used to refine the SYNGAS from gasifier and a bypass line to control the composition of SYNGAS at the exit of cascade reactor as shown in Fig. 1.

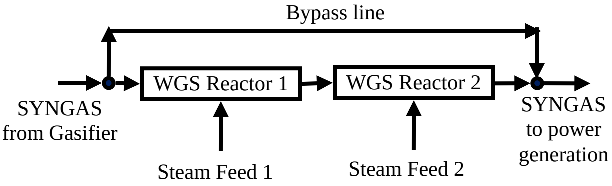

Figure 1. Schematic view of cascade WGS reactor system

During the first stage, SYNGAS from the gasifier is fed into the system and mixed with steam at the WGS Reactor 1. The composition of SYNGAS from the gasifier is assumed to be known and given in Table 2. Some portion of the SYNGAS from the gasifier is mixed with the exiting stream via bypass line connecting inlet and exit streams. During the second stage, SYNGAS at the exit of WGS Reactor 1 is mixed with a second stream of steam. SYNGAS at the exit of WGS reactor 2 is mixed with a bypass stream to produce resulting composition. The SYNGAS refinement process can be controlled by adjusting the SYNGAS bypass ratio, f, and the steam to SYNGAS ratios, SR_1 and SR_2.

3. SOLUTION METHODOLOGY

The variation of the equilibrium constant with temperature for the WGS reaction is given in Table 1. An interpolation routine is implemented in the cascade WGS reactor model to compute the equilibrium constant, $K_{p,s}$of the WGS reaction at the intermediate temperatures. The gas compositions from the gasifier model are used as the input conditions to compute the output concentrations of the first shift reactor based on WGS reaction equilibrium, which are then used as the input conditions to compute the output of the second shift reactor again based on WGS reaction equilibrium. Calculation steps in the cascade WGS reactor model is introduced as flowchart in Figure 2.

Table 1. Variation of equilibrium constant, $K_{p,s}$with temperature for the WGS reaction [2]

Temperature (K)	$K_{p,s}$
400	4050.00
600	27.00
800	4.04
1000	1.38
1500	0.37

According to the flowchart, the model requires SYNGAS composition to be known at the beginning of calculation and after entering the operation parameters such as the steam ratios, SR_1 and SR_2, reactor temperatures, T_1 and T_2, and the H_2/CO ratio to be expected, the model performs calculations for SR_1 and SR_2. If the calculations converged to a solution, the program save the results to a file and stops. Otherwise perform the following operations; updating the values of SR_1 and SR_2 and giving an initial value to the bypass ratio, the WGS reaction is solved to get a SYNGAS composition. As a final step, the desired H_2/CO ratio is checked. If this ratio

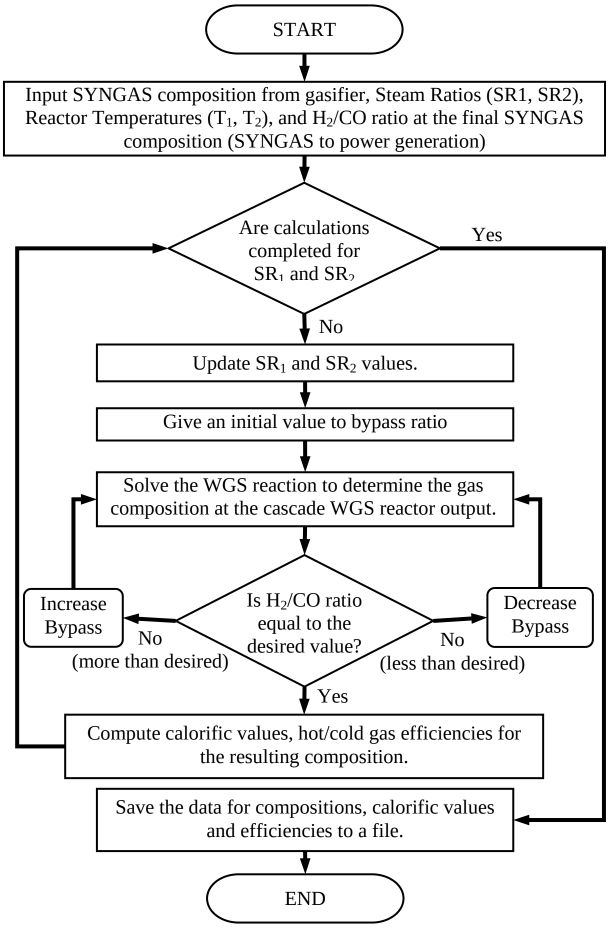

Figure 2. Flowchart of cascade WGS reactor model

satisfies the criteria, the program computes the HHV of the resulting SYNGAS composition, hot and cold gas efficiencies of the system.

4. RESULTS

There are six parameters effecting the SYNGAS composition; ratios of steam-1 to SYNGAS, SR_1 and steam-2 to SYNGAS, SR_2, temperatures of WGSR-1, T_1 and WGSR-2, T_2, operating pressure, P and bypass ratio, f.

Fig. 3 shows the effect of operating pressure on SYNGAS composition. As it is seen from the Fig.3, H_2/CO ratio increases with operating pressure. On the other hand SYNGAS WGS reactor output composition does not change considerably with operating pressure. Therefore, operating pressure can be chosen as atmospheric pressure in the refinement process.

Fig. 4 shows that the temperature of the first WGS reactor has no effect on the output syngas composition. This is expected because the temperature of the second WGS reactor determines the final equilibrium concentrations of the gases participating in the shift reaction. Since the amount of steam fed to the system and the second reactor's temperature are the same for all cases, the resulting gas composition is the same regardless of the temperature of the first WGS reactor.

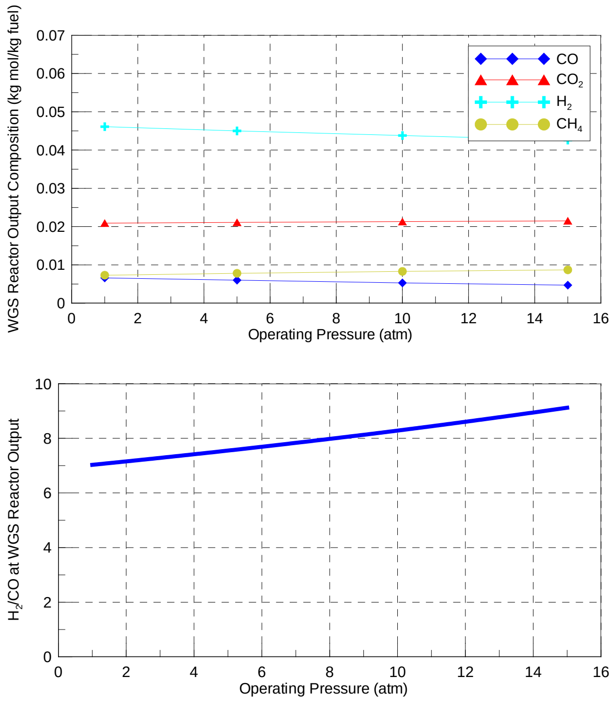

Fig. 3. Effect of operating pressure on SYNGAS composition and H_2/CO (T_1 = 350 °C, T_2 = 200 °C, bypass = 0, SR_1 = 0.3, SR_2 = 0).

Fig. 5 shows that increasing the temperature of the second WGS reactor reduces the amount of H2, and increases that of CO in the output, since the shift reaction is exothermic. Consequently, the H2/CO is lower at higher temperatures.

Figs. 6 and 7 show the variation of molar ratio of steam-1 to SYNGAS, SR_1 and steam-2 to SYNGAS, SR_2. It can be observed that it does not make noticeable difference whether the steam is fed into the first or second WGS reactor. It can also be seen that increasing the amount of steam fed increases the amount of H2 produced at first, but reaches a saturation value around $SR_1 = 0.5$. Hence this is the optimal value of the steam molar ratio to be used in the process. Increasing SR_1 further seems to increase the H2/CO ratio but in reality this increase is irrelevant because it is not caused by a significant increase in H2 concentration but instead by the CO concentration approaching zero and hence the H_2/CO ratio increasing indefinitely.

Fig. 8 shows the effect of bypass ratio on SYNGAS WGS reactor output composition. As shown from Fig. 8, H_2/CO ratio decreases from 7 to 1 when the bypass ratio increases from 10% to 90%. It all depends on the purpose of further use of the SYNGAS.

The bypass ratio can be optimized to achieve a desired SYNGAS composition. We assume that the composition of the SYNGAS from gasifier is known at the beginning

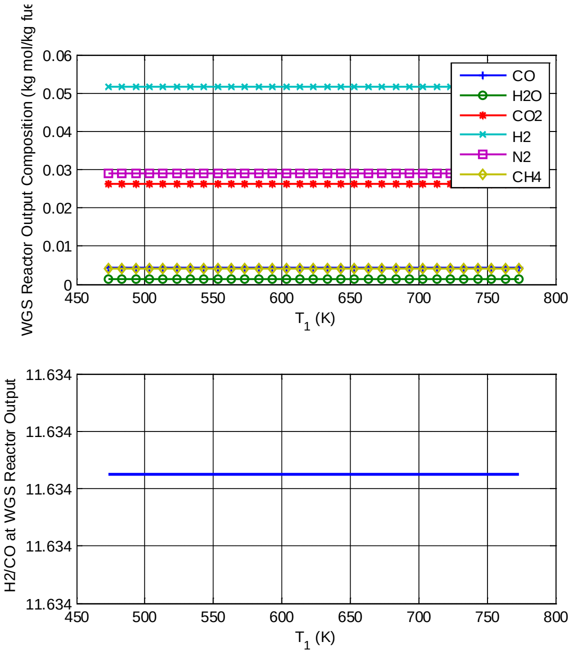

Fig. 4. Effect of the temperature of WGSR-1, T_1 on SYNGAS composition (T_2 = 200°C, bypass = 0, SR_1=0.3, SR_2 = 0)

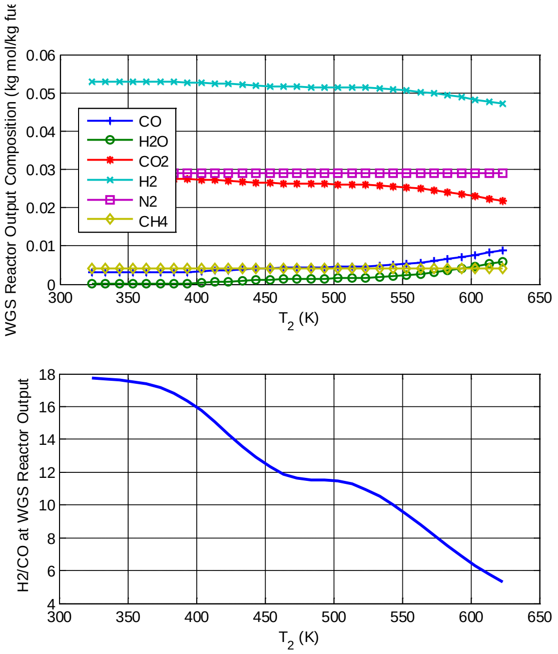

Fig. 5. Effect of the temperature of WGSR-2, T_2 on SYNGAS composition and H_2/CO ratio (T_1 = 350 °C, bypass = 0, SR_1=0.3, SR_2 = 0)

of refinement process. Based on the results on the determination of the temperature of WGSR-1 and 2, the temperature of the first reactor is selected as 350°C, and that of the second reactor is 200°C. Eleven attempts are performed while varying SR_1 and SR_2 from 1 to 0 with increments of 0.1. For each case, the optimal bypass ratio is computed to give a H_2/CO ratio of 2 at the end of refinement process using the algorithm shown in Figure 2, which turns out to be close to 0.61 for all cases.

The results are tabulated in Table 3, along with the output gas compositions, as well as the hot gas efficiency, η_h and cold gas efficiency, η_c of the product SYNGAS, which are defined as follows:

$$\eta_c = \frac{HHV_{syngas}}{HHV_{fuel}} \tag{1}$$

$$\eta_h = \frac{(HHV + \Delta \mathrm{H})_{\mathrm{syngas}}}{HHV_{fuel}} \tag{2}$$

The heating value of the SYNGAS is computed from the sum of heating values of individual combustible constituents, which are H_2, CO, CO_2, H_2S and CH_4. The data for the heating values and enthalpies of these gases at various temperatures are readily available in many references [2]. For this case the amount of H_2S and CH_4 are negligible and therefore have not been included in the calculations of heating value. Looking at Table 3 one can observe that the desired H_2/CO ratio of 2 is achieved for all cases. In addition, one observes that the results are very close to each for all cases of SR_1 and SR_2. This suggests that the process is not very sensitive to individual amounts of steam fed to WGS1 and WGS2 reactors, and the important point is the total amount of steam fed. Therefore to simplify our analysis for the case

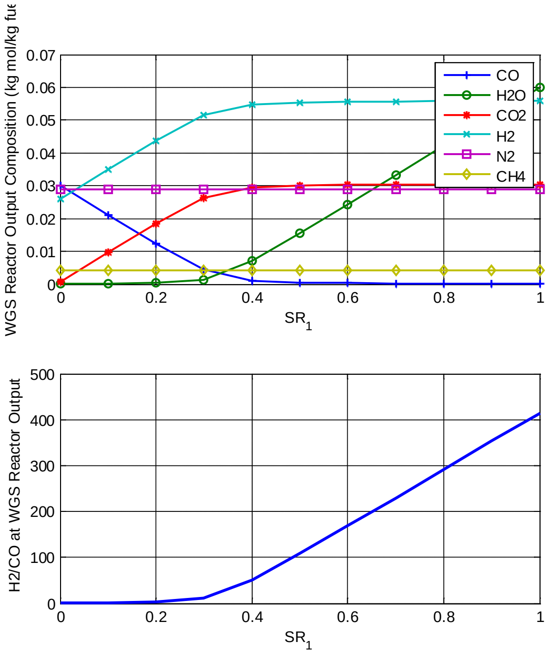

Fig. 6. Effect of the molar ratio of steam-1 to SYNGAS, SR_1 on SYNGAS composition (T_1 = 350 °C, T_2 = 200 °C, bypass = 0, SR_2 = 0)

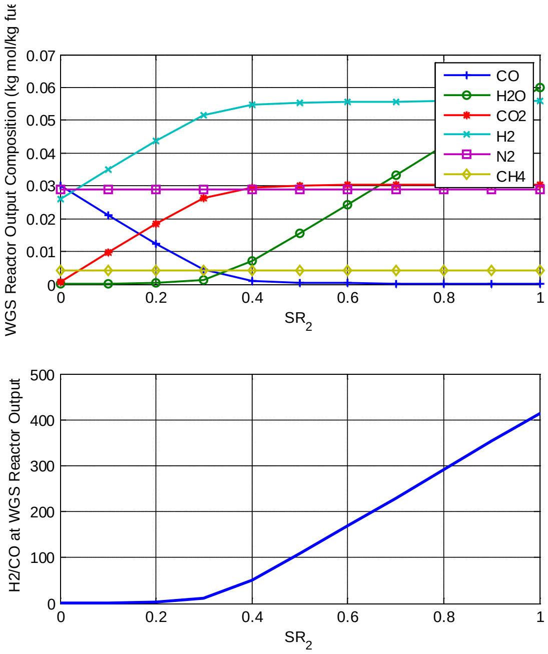

Fig. 7. Effect of the molar ratio of steam-2 to SYNGAS, SR_1 on SYNGAS composition (T_1 = 350 °C, T_2 = 200 °C, bypass = 0, SR_1 = 0)

to be discussed next, we shall assume that all the steam is fed to the first reactor.

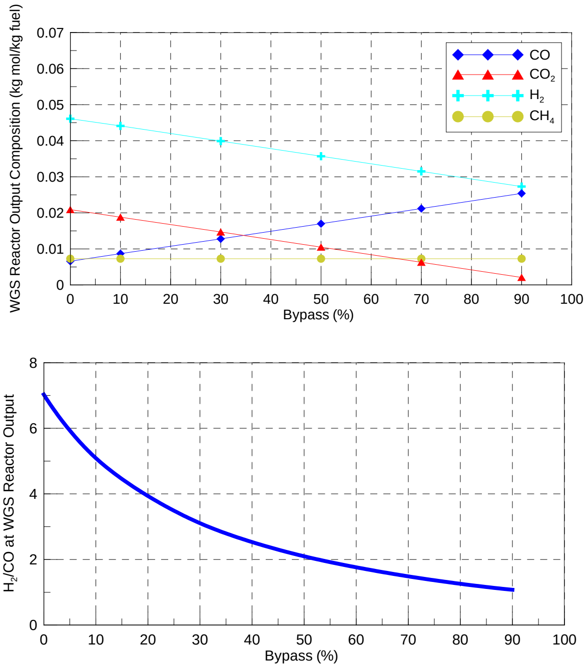

Fig. 8. Effect of bypass ratio on SYNGAS composition and H_2/CO ($T_1 = 350\,^{o}C$, $T_2 = 200\,^{o}C$, $SR_1 = 0.3$, $SR_2 = 0$).

For the next case we determine the minimal amount of steam to be fed to the WGS reactors to achieve $H_2/CO = 2$ under different bypass values. We follow the same procedure as described in Figure 2, but the parameter optimized is SR_1. The results are tabulated in Table 4. Observing the results in the table one notes that the minimal amount of steam is required when the bypass ratio is zero. This is understandable since the amount of CO going into the WGS reactors is the highest for this case and hence the required amount of H_2 can be produced with less amount of steam. The attempts for bypass ratio higher than 0.65 do not yield a feasible solution and hence are not shown in the table. This is expected since if the bypass ratio is very high, most of the gas is bypassed directly to the output. Thus, very little CO is left in the gas going into the WGS reactors, from which a sufficient amount of H_2 cannot be synthesized to achieve the desired H_2/CO ratio of 2.

5. CONCLUSION

It can be concluded from this study that the operating pressure should be atmospheric for the refinement process. There are three important parameters to control the composition of SYNGAS; steam ratios, temperature of the second WGS reactor and bypass ratio. It is observed that the optimum value of H_2/CO in the SYNGAS composition for any combination of parameters depends on the purpose of the final use aimed. Therefore, it is judged in the view of experience that it should be sufficient to take the value of H_2/CO as 2 in the SYNGAS produced for methanol production as a case study. Then, the amount of SYNGAS is determined depending on the ratio of SR_1 to SR_2. Analyzing the optimization results, it is concluded that the amount of SYNGAS produced should be kept about 0.13 kmol per 1 kg of fuel for any ratio of SR_1 to SR_2 and the value of 2 for H_2/CO. As a general conclusion, it can be said that there is only one appropriate value for the amount of SYNGAS produced corresponding to each H_2/CO value.

Table 2. The composition of SYNGAS from gasifier*

SYNGAS Composition	**Mass Percentage (%)**
H_2	28,55
CO	33,71
CO_2	0,37
N_2	32,28
H_2O	0,40
CH_4	4,69
Total	100,00
H_2 / CO	0,846879

* A/F = 1, S/F = 0.1, P = 1 atm and T = 1150 K

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Table 3. Gas composition, cold and hot gas efficiencies at the output of the two stage WGS reactor for different steam feed ratios for the first and second WGS reactors. The bypass ratio necessary to achieve H2/CO=2 is calculated to be 0.61 for all cases.

SR_1	**SR_2**	$\dot{n}_{SYNGAS}$	**H_2**	**CO**	**CO_2**	**N_2**	**H_2O**	**H_2/CO**	η_c	η_h
		[kmol]	**[%]**	**[%]**	**[%]**	**[%]**	**[%]**			
1.0	0.0	0.1245	29.95	14.97	9.62	23.28	18.79	2.00	0.82	0.85
0.9	0.1	0.1276	29.22	14.61	9.38	22.72	20.76	2.00	0.82	0.85
0.8	0.2	0.1300	28.68	14.34	9.21	22.30	22.24	2.00	0.82	0.85
0.7	0.3	0.1317	28.30	14.15	9.09	22.00	23.25	2.00	0.82	0.85
0.6	0.4	0.1328	28.08	14.04	9.02	21.83	23.85	2.00	0.82	0.85
0.5	0.5	0.1331	28.01	14.00	8.99	21.78	24.05	2.00	0.82	0.85
0.4	0.6	0.1328	28.08	14.04	9.02	21.83	23.85	2.00	0.82	0.85
0.3	0.7	0.1317	28.30	14.15	9.09	22.00	23.25	2.00	0.82	0.85
0.2	0.8	0.1300	28.68	14.34	9.21	22.30	22.24	2.00	0.82	0.85
0.1	0.9	0.1276	29.22	14.61	9.38	22.72	20.76	2.00	0.82	0.85
0.0	1.0	0.1245	29.95	14.97	9.62	23.28	18.79	2.00	0.82	0.85

Table 4. Gas composition, cold and hot gas efficiencies at the output of the two stage WGS reactor for different bypass rates and steam feed ratios for the first WGS reactor (SR_1). SR_2 is zero for all cases.

SR_1	**f**	$\dot{n}_{SYNGAS}$	**H_2**	**CO**	**CO_2**	**N_2**	**H_2O**	**H_2/CO**	η_c	η_h
		[kmol]	**[%]**	**[%]**	**[%]**	**[%]**	**[%]**			
0.13	0.00	0.1012	36.84	18.42	11.83	28.64	0.11	2.00	0.82	0.84
0.14	0.07	0.1012	36.82	18.41	11.82	28.63	0.14	2.00	0.82	0.84
0.15	0.14	0.1013	36.81	18.41	11.82	28.62	0.18	2.00	0.82	0.84
0.16	0.20	0.1013	36.80	18.40	11.82	28.61	0.21	2.00	0.82	0.84
0.18	0.27	0.1014	36.78	18.39	11.81	28.60	0.26	2.00	0.82	0.84
0.20	0.34	0.1014	36.76	18.38	11.80	28.58	0.31	2.00	0.82	0.84
0.22	0.41	0.1015	36.74	18.37	11.80	28.56	0.38	2.00	0.82	0.84
0.25	0.47	0.1016	36.70	18.35	11.78	28.53	0.49	2.00	0.82	0.84
0.29	0.54	0.1019	36.59	18.30	11.75	28.45	0.77	2.00	0.82	0.84
0.53	0.61	0.1085	34.38	17.19	11.04	26.73	6.78	2.00	0.82	0.85