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**ITER TASK T299 (1995):  
HITEX Demonstration Tests**

**CFFTP G-9602  
January, 1996**

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## 1. TASK OBJECTIVES

The objective of this task is to demonstrate processes for efficient cleanup and detritiation of the plasma exhaust. In this subtask, the objectives were to provide further design data on the HITEX process, and to build and demonstrate 2-stage high-detritiation HITEX performance.

## 2. BACKGROUND

The original HITEX concept proposed for detritiating impurities in the ITER plasma exhaust was based on a batch process that uses catalyst-assisted isotopic exchange of tritium bound to impurities with protium and extraction of the resulting elemental tritium with a permeator [1, 2]. The main advantage of this process is that it is simple, does not produce tritiated water and is capable of achieving high detritiation factors (DFs).

Following successful proof-of-principle tests at Ontario Hydro [3], preliminary tritium tests were carried out at Chalk River Laboratories (CRL) with tritiated methane (CQ<sub>4</sub>, Q = H, D or T) and mixed CQ<sub>4</sub>/He mixtures under ITER Task T49 in 1994 [4, 5].

In the batch-HITEX process, impurity detritiation is characterized by an initial fast-detritiation step followed by a slow-detritiation step. The slow-detritiation step, which is detrimental to the overall detritiation process, is consistent with the process, being limited by the slow desorption of tritium from contaminated surfaces. Under the conditions tested in 1994, ~99.99-99.999% of the initial activity was removed in the fast-detritiation step corresponding to DF in the range  $1 \times 10^4$ - $1 \times 10^5$ . At higher DFs ( $> 1 \times 10^5$ ), the detritiation rate slows down consistent with a slow surface-outgassing process. The dominant sources contributing to this slow degassing process were not conclusively identified in the 1994 program.

A simple model was developed to describe the HITEX process based on the following simplifying assumptions:

1. complete mixing of gases,
2. complete isotopic equilibrium of hydrogen isotopes among gases at the outlet of the reactor, and
3. constant, isotope-independent hydrogen isotopes recovery fraction of the permeator.

From a simple mass balance for tritium in the tank, the DF can be shown to be given by:

$$DF = e^{\lambda t} \quad (1)$$

$$1 = [f_{\text{perm}} Q_L / (V_{\text{imp}} (1+R))] [f_{Q2} + R / (f_{Q2\text{eq}} + R)] \quad (2)$$

where:

- $Q_L$  is the loop recirculation flow rate at the operating conditions (L/min),  
 $R$  is the molar ratio  $V_{H_2}/V_{imp}$  (where  $V_{H_2}$  is the tritium-free hydrogen added to the tank initially and  $V_{imp}$  is the number of impurity moles in the tank),  
 $f_{perm}$  is the isotope-independent hydrogen isotopes recovery fraction of the permeator,  
 $f_{Q_2}$  is the mole fraction of  $Q_2$  gas present initially in the impurities  $V_{imp}$ , and  
 $f_{Q_2eq}$  is the mole fraction of equivalent  $Q_2$  in  $V_{imp}$ .

According to the model, under complete isotopic equilibration in the reactor and perfect mixing conditions, the DF is a simple exponential function of time with the pre-exponential factor  $\lambda$  determining the detritiation rate. The model was shown to be consistent with the fast-detritiation step and agreed well with the observations: DF increased with  $Q_L$ , DF increased with  $R$ , and no initial tritium concentration effects. The model was found to agree well with the experimental data at high recirculation flow rates (5 L/min (STP) while underpredicting at lower flow rates (2 L/min (STP))). This was attributed to poor mixing conditions in the tank (perfect plug flow conditions would keep the reactor feed at the highest possible tritium concentration) that would increase the average detritiation rate.

### 3. EXPERIMENT DESCRIPTION

#### 3.1 Experimental Setup

The experimental facility is located in the Tritium Laboratory at CRL. A schematic diagram of the batch-HITEX loop is given in Figure 1. Detailed descriptions of the loop and its components are given in References 4 and 5.

The single-pass front end and a second tank was added to the loop for the two-stage HITEX demonstration tests. A schematic diagram of the two-stage HITEX loop is shown in Figure 2. The catalyst reactor and the permeator (RSD Model 50) used in the single-pass front-end were similar to the ones used in the batch loop.

In 1995, experiments were carried out under humid gas conditions up to ~50% relative humidity. At the outlet of the permeator, the gas is enriched with impurities and can lead to water vapor condensation. To avoid water vapor condensation at the outlet of the permeator, these areas were heat traced to 80-100°C. The heated areas are shown with thick solid lines in Figures 1 and 2.

#### 3.2 Experimental Procedures

The batch-HITEX loop operating procedures are described in detail in References 4 and 5. The two-stage tests were carried out with ITER relevant gas mixtures. The single-pass front end was operated with a gas mixture containing 5% impurities in  $H_2$  ( $R = 19$ ) and at a total flow rate of 460 mL/min(STP). The batch loop was operated with a gas mixture containing 25% of impurities in  $H_2$  ( $R = 3$ ) at a recirculation flow rate of 5 L/min. The

required gas composition in the front-end was prepared by mixing appropriate amounts of the tritiated methane gas with H<sub>2</sub> and He. For tests under humid conditions, the He gas was humidified by passing through a water bubbler maintained at an appropriate temperature.

The tritium concentration in the feed to the reactor and the permeator bleed were measured with ionization chambers. The reactor and the permeator in the front-end were operated at 400°C and 425°C respectively. The tritium removed in the front-end through the permeator was pumped into a Ti getter bed and the permeator bleed was used to fill one of the two 15 L tanks while the content in the other tank was being processed. In the preliminary two-stage HITEX tests, a two-hour batch-cycle was used. At the end of a batch-HITEX cycle, the tank was isolated and the detritiated gas mixture in the tank was evacuated and vented. The empty tank was then switched over to the fill-side to accept the permeator bleed and the filled tank was switched to the batch-processing side manually.

## 4. RESULTS

### 4.1 Effect of Operating Parameters

#### 4.1.1 Effect of Catalyst Temperature

In these experiments, a catalytic reactor containing 120 g of 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was used. The effect of temperature on the batch-HITEX performance was investigated in the temperature range 300–400°C using the standard gas mixture (4% CQ<sub>4</sub>/H<sub>2</sub>). The run parameters are listed in Table 1.

Table 1 - Effect of Temperature on HITEX Performance - Run Conditions

Run#	Flow L/min (STP)	Temperature (°C)		Initial Tritium Activity (Ci/m <sup>3</sup> )
		Catalyst	Permeator	
10	2	350	425	67
12	2	300	425	64
13	2	400	425	66.5

Figure 3 shows the effect of temperature on DF. At 300°C, the detritiation rate in the fast-detritiation step is significantly lower compared to the rates observed at higher temperatures (>350°C). A significant change in the detritiation rate was not observed when the temperature was increased from 350°C to 400°C.

According to the simple model (Equations 1 and 2), the detritiation rate is determined by  $\lambda$ . The difference between experimental ( $\lambda_{exp}$ ) and model ( $\lambda_{mod}$ )  $\lambda$  values represent the extent of the system's departure from complete mixing and equilibrium conditions under

the operating conditions. The system's departure from the ideal conditions was quantified using an empirical constant  $k$  defined by:  $k = \lambda_{\text{exp}}/\lambda_{\text{model}}$ . The value of  $k$  approaches 1 as the system approaches ideal mixing and complete equilibrium conditions. Under complete equilibrium but poor mixing conditions, The value of  $k$  must become greater than 1, and under perfect mixing but incomplete equilibrium conditions,  $k$  must become less than 1. Table 2 shows the  $k$  values calculated from experimental data for the runs at different catalyst temperatures.

Table 2 - Effect of Temperature on HITEX Performance - Results

Run#	Catalyst Temperature (°C)	k
10	350	1.28
12	300	0.78
13	400	1.36

At the same flow rate (similar mixing conditions in the loop), the value of  $k$  is significantly lower than 1 at 300°C indicating that complete isotopic equilibrium is not reached at the outlet of the reactor at this temperature. At temperatures above 350°C,  $k$  is significantly greater than 1 and a further increase in the catalyst temperature from 350°C to 400°C did not significantly change the value of  $k$ . These data appear to suggest that complete isotopic equilibrium is approached at temperatures >350°C at the reactor outlet. These data are consistent with the results of the proof-of-principle tests carried out with a 4% CD<sub>4</sub>/H<sub>2</sub> gas mixture [3]. In these tests, the isotopic equilibrium was shown to reach at temperatures >375°C with 120 g of catalyst at 2 L/min (STP). According to the data, a reactor operating temperature of 400°C is probably a minimum to ensure complete isotopic equilibrium at the reactor outlet with the present catalyst bed (120 g, ~100 m<sup>2</sup>/g) for the 4% CQ<sub>4</sub>/H<sub>2</sub> gas mixture.

#### 4.1.2 Effect of Loop Pressure

The effect of the loop pressure on the HITEX performance was investigated very briefly. The run conditions are listed Table 3 and the results are shown in Figure 4. The experimental data show a slight deterioration in the performance when the loop pressure was increased to 1000 torr (permeator was unchanged at 1000 torr in both cases).



Table 3 - Effect of Loop Pressure - Run Conditions

Run #	Loop Flow L(STP)/min	Loop Pressure (Torr)	Temperature (°C)		Initial Tritium Activity (Ci/m <sup>3</sup> )	Gas Composition (%)	
			Catalyst	Permeator		CQ <sub>4</sub>	H <sub>2</sub>
11	2	1000	400	425	66.5	4	96
13	2	760	400	425	66.5	4	96

#### 4.1.3 Effect of Gas Residence Time in the Catalyst Bed

The effect of gas residence time on the HITEX performance was investigated for different gas compositions. These tests were carried out using a small catalyst bed containing 21g of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. The test-run conditions are given in Table 4.

Figure 5 shows the effect of flow rate on the detritiation rate. In the fast-detritiation region, the detritiation rate as indicated by the slope of the curve shows an increase with the recirculation flow rate from 1 to 3 L/min. In the flow rate range 3 - 4.5 L/min(STP), the detritiation rate remained relatively constant and decreased at higher flow rates (>4.5 L/min(STP)). Figure 6 compares the initial detritiation rates for the two catalyst beds (21 and 120 g) at the same recirculation flow rate (2 L/min) for three different CQ<sub>4</sub> concentrations in the gas. Although the gas residence time is smaller in the short (21 g) catalyst bed at 2 L/min, the detritiation rates are similar with both beds and depended little on the CQ<sub>4</sub> concentration in the gas.

Table 4 - Effect of Residence Time - Run Conditions

Run#	Loop Flow L(STP)/min	Temperature (°C)		Initial Tritium Activity (Ci/m <sup>3</sup> )	Gas Composition (%)	
		Catalyst	Permeator		CQ <sub>4</sub>	H <sub>2</sub>
24	5.0	400	425	94.7	4	96
25	2.0	400	425	92.5	4	96
26	3.0	400	425	92.9	4	96
27	4.0	400	425	94.7	4	96
28	4.5	400	425	92.9	4	96
29	1.0	400	425	91.6	4	96
30	2.5	400	425	93.8	4	96
31	2.0	400	425	100.2	30	70
32	2.0	400	425	92.1	70	30
33	3.0	400	425	98.8	30	70
34	4.0	400	425	101.4	30	70

Figure 7 compares the detritiation rates for the two catalyst beds at 5 L/min for the 4% CQ<sub>4</sub>/H<sub>2</sub> gas mixture. At 5 L/min, the initial detritiation rate is significantly smaller with the short bed, indicating poor HITEX performance at short residence times<sup>1</sup>.

The effect of residence time on the detritiation rate was evaluated by estimating  $k$  for all experiments. The  $k$  values are listed in Table 5 as a function of the flow rate along with linear velocity and residence time data. Figure 8 shows a plot of  $k$  as a function of the flow rate for different gas mixtures.

With the 4% CQ<sub>4</sub>/H<sub>2</sub> mixture, at long residence times (>72 ms) or low flow rates (<3 L/min (STP)), the value of  $k$  is significantly higher than 1 indicating poor mixing conditions in the loop. The value of  $k$  is unaffected (~1.32) when the residence time was increased from 108 ms (see Table 4, Run# 25 short bed) to 603 ms (see Table 4, Run# 8, long bed) at the same flow rate. These data appear to suggest that close to complete equilibrium conditions are reached at residence times >72 ms. However, Figure 8 and Table 5 clearly show that complete equilibrium conditions are not reached with gas mixtures containing 30% and 70% CQ<sub>4</sub> even at gas residence times as high as 603 ms ( $k < 1$ ). It is possible that a much larger catalyst bed, than the 120 g bed used currently is required to reach complete equilibrium conditions at high CQ<sub>4</sub> contents under practical recirculation flow rates.

According to the data, the optimum HITEX performance is reached at gas residence times >~108 ms for the 4% CQ<sub>4</sub>/H<sub>2</sub> gas mixture. At 1 L/min, although the gas residence time is significantly higher than the minimum residence time, the lower  $k$  value observed appears to indicate far from isotopic equilibrium conditions at the reactor outlet. It is possible that external mass transfer limitations are responsible for poor isotopic equilibrium conditions at low linear gas velocities. Therefore, it is probably important to operate at sufficiently high linear velocities (>0.24 m/s) and residence times (>108 ms) to obtain high detritiation rates.

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<sup>1</sup> Although the initial detritiation rate was smaller for the short bed, the DF achieved after 60 minutes of operation was the same for both beds. Also, with the large bed, the turnover from the fast- to slow-detritiation rates occurred considerably early at a DF of ~ $1 \times 10^3$  compared to ~ $1 \times 10^4$  for the short bed. These data are consistent with the catalyst being the contamination source responsible for the slow-detritiation step. This is discussed in detail in Section 4.4.

Table 5 - Effect of Residence Time - Test Results

Run#	Flow Rate (L/min)	Composition	Linear Velocity (m/s)	Residence Time (ms)	$\lambda_{exp}$	$\lambda_{model}$ (Average)	k
Short Bed (21 g Catalyst)							
29	1	4%CQ <sub>4</sub> /H <sub>2</sub>	0.24	216	0.0523	0.0478	1.09
25	2	4%CQ <sub>4</sub> /H <sub>2</sub>	0.47	108	0.1476	0.1104	1.34
30	2.5	4%CQ <sub>4</sub> /H <sub>2</sub>	0.60	86	0.1891	0.1515	1.25
26	3	4%CQ <sub>4</sub> /H <sub>2</sub>	0.71	72	0.2332	0.1818	1.28
27	4	4%CQ <sub>4</sub> /H <sub>2</sub>	0.96	54	0.2435	0.2393	1.02
28	4.5	4%CQ <sub>4</sub> /H <sub>2</sub>	1.07	50	0.2388	0.2511	0.95
24	5	4%CQ <sub>4</sub> /H <sub>2</sub>	1.20	45	0.2024	0.2532	0.78
31	2	30%CQ <sub>4</sub> /H <sub>2</sub>	0.47	108	0.0542	0.0666	0.81
33	3	30%CQ <sub>4</sub> /H <sub>2</sub>	0.71	72	0.0763	0.1009	0.76
34	4	30%CQ <sub>4</sub> /H <sub>2</sub>	0.96	54	0.0793	0.1165	0.68
32	2	70%CQ <sub>4</sub> /H <sub>2</sub>	0.47	108	0.0125	0.0178	0.70
Long Bed (120 g Catalyst)							
8	2	4%CQ <sub>4</sub> /H <sub>2</sub>	0.47	603	0.1489	0.1124	1.32
5	2	30%CQ <sub>4</sub> /H <sub>2</sub>	0.47	603	0.0556	0.0678	0.82
7	2	70%CQ <sub>4</sub> /H <sub>2</sub>	0.47	603	0.0149	0.0193	0.77
4	5	4.9%CQ <sub>4</sub> /H <sub>2</sub>	1.20	243	0.2670	0.3016	0.88

## 4.2 Effect of Impurities on Detritiation Factor

### 4.2.1 Effect of Non-Tritium Containing Impurities in the Gas

Various impurity gases other than organics such as inert gases, CO, CO<sub>2</sub> and H<sub>2</sub>O vapor are expected to be present in the fusion-fuel exhaust. The effect of inerts were briefly investigated in the 1994 HITEX program. This year, experiments were carried out to determine the effect of oxygen containing gases such as CO and CO<sub>2</sub> on the HITEX performance. The experimental run conditions are given in Table 6.

The experimental results are shown in Figure 9. Addition of CO and CO<sub>2</sub> had a significant effect on the detritiation performance. The detritiation rate in the fast-detritiation region (or  $\lambda$ ) decreased with the impurity concentration indicating that complete isotopic equilibrium is not reached in the reactor when impurities such as CO and CO<sub>2</sub> are present in the gas. Also the final DF that can be achieved after a given processing period decreased with the increasing impurity concentration in the gas for both impurities.

Table 6 - Effect of CO and CO<sub>2</sub> (Experimental Conditions)

Run#	Loop Flow L(STP)/min	Temperature (°C)		Initial Tritium Activity (Ci/m <sup>3</sup> )	Gas Composition (%)		
		Catalyst	Permeator		CQ <sub>4</sub>	CO	H <sub>2</sub>
35	2	400	425	97.3	4	1	95
36	2	400	425	93.1	4	3	93
					CQ <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub>
37	2	400	425	94.2	4	1	95
38	2	400	425	93.6	4	3	97
39	2	400	425	92.3	4	3	97

With both impurity gases water vapor is formed in the system by methanation reactions:



The poor isotopic equilibration in the reactor may have been caused by the competition of methanation reactions with the isotopic exchange reactions for the active sites, initially in the process. The water vapor formed by methanation of CO and CO<sub>2</sub> is partially tritiated and because of its strong adsorption on surfaces, the overall poor detritiation performance can be attributed to the poor transport of water vapor in the system.

#### 4.2.2 Effect of H<sub>2</sub>O Vapor

Water vapor is considered as a common impurity that may be present in the fusion-fuel exhaust. The effect of water vapor in the system was investigated up to ~50% relative humidity (RH) in the tank. The experiments were carried out with the standard gas mixture (4% CQ<sub>4</sub>/H<sub>2</sub>) with an initial tritium activity of ~100 Ci/m<sup>3</sup>. The experimental run conditions are given in Table 7.

Figure 10 compares the results from Run#40 and Run#41 obtained under humid conditions, with the results from a dry run. In Run#40, the loop was first humidified with a moisture saturated H<sub>2</sub> purge stream before the run and water vapor was not added to the system during the run. In this case, the dew point of the loop gas decreased from about +30°C (the box temperature was +32°C) to -10°C during the run. In Run#41, water vapor was added to the system continuously with hydrogen and the dew point of the gas was maintained at 17°C. The decrease in the dew point during the run in the first case, and the large amount of water vapor needed to add to the loop to maintain the dew point constant in the second case, suggest a loss of water vapor from circulation probably due to condensation in some parts of the loop. And the permeator outlet, the bleed gas is enriched with impurities and water vapor due to hydrogen permeation and as a result can lead to water vapor condensation. To avoid vapor condensation in subsequent runs, the

Table 7 - Effect of Water Vapor - Test Conditions

(The standard 4% $\text{CQ}_4/\text{H}_2$  gas was used in all experiments unless otherwise specified)

Run#	Loop Flow L(STP) /min	Temperature (°C) Cat./Perm	Comments
40	2	400/425	water vapor was added only initially dew point decreased from +30°C to -10°C lines downstream of the permeator were not heated
41	2	400/425	water vapor added continuously to the loop dew point: +17°C (constant) lines downstream of the permeator were not heated
45	2	400/425	water vapor added after the turnover point from fast to slow detritiation lines downstream of the permeator were heated (80-100°C) dew point: -26°C (initial)/-4°C (final)
48*	2	400/425	water vapor added after the turnover point from fast to slow detritiation lines downstream of the permeator were heated (80-100°C) dew point: -23°C (initial)/-4°C (final)
49	5	400/425	water vapor added after the turnover point from fast to slow detritiation lines downstream of the permeator were heated (80-100°C) dew point: -15°C (initial)/9°C (final)

\* the gas composition in the run was 33.3% $\text{CQ}_4/33.3\%\text{He}/33.3\%\text{H}_2$ 

lines downstream of the permeator were kept at elevated temperatures (80-100°C). The heated zones are shown in thick lines in Figures 1 and 2.

In Run#45 and Run#49, water vapor was added to the loop only after the transition from fast to slow detritiation. It was assumed that the desorption of the surface-adsorbed tritium responsible for the slow detritiation process could be enhanced by swamping with water vapor. Figure 11 compares the results from Run#49 with those obtained under dry conditions (Run#4) carried out under identical operating conditions.

As Figure 11 shows, the addition of water vapor after the transition from fast to slow detritiation did not improve the detritiation rate in the slow-detritiation region compared to the rates observed under dry conditions. These data appear to suggest that the surface-

adsorbed tritium responsible for the slow detritiation step is not in the form of adsorbed water.

Eliminating vapor condensation in the loop improved the HITEX performance significantly. In the presence of water vapor in the loop, the detritiation rate in the fast-detritiation region was slower and the final DF attained was significantly lower compared to dry runs. In Run#49, the final DF achieved after 120 min of operation is  $\sim 3 \times 10^4$ , well below the design target of  $1 \times 10^5$ .

#### 4.3 Performance of Ni/Kieselghur Catalyst

Ni/Kieselghur catalyst is used both as a cracking and isotopic exchange catalyst in the CAPRICE (Catalytic Purification Experiment) loop at FzK (Research Center Karlsruhe). The Ni/Kieselghur catalyst was investigated as a possible alternative catalyst for the HITEX process. As with the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, 120 g of the Ni/Kieselghur catalyst was used in the reactor. The experimental conditions are listed in Table 7.

The experimental results from these tests are compared with the results obtained with the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst under similar operating conditions in Figure 12. The tests with the Ni/Kieselghur catalyst were found to be difficult to reproduce. Although results were reproducible in the fast-detritiation region, different catalyst treatments led to notable changes in the slow-detritiation region.

Table 8 - Ni/Kieselghur Catalyst Performance - Run Conditions

(The standard 4% CQ<sub>4</sub>/H<sub>2</sub> gas was used in all experiments unless otherwise specified)

Run#	Loop Flow L(STP)/min	Temperature (°C) Cat./Perm	Initial Tritium Activity (Ci/m <sup>3</sup> )	Comments
16	2	400/425	487.0	catalyst activated 7 h in H <sub>2</sub>
17	2	400/425	46.0	catalyst activated 7 h in H <sub>2</sub>
18	2	400/425	99.0	additional 5 h reduction in H <sub>2</sub>
19	2	400/425	94.2	loop heated/evacuated for 8 h
20	2	400/425	89.5	H <sub>2</sub> circulated/loop evacuated x2
21	2	400/425	695.0	10 Ci

The detritiation rates in the fast-detritiation region ( $\lambda$ ) were found to be similar for both Ni/Kieselghur and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts at 2 L/min (STP). These data appear to suggest that complete isotopic equilibrium is reached in the reactor under the operating conditions used. Also different catalyst pretreatments had little effect on  $\lambda$  indicating little effect of these treatments on the catalyst activity. However, the transition from fast to slow detritiation occurred at a much lower DF ( $\sim 2 \times 10^2$ ) with the Ni/Kieselghur catalyst compared to  $\sim 1 \times 10^3 - 1 \times 10^4$  with the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. The Ni/Kieselghur catalyst

appears to retain (adsorb) significantly more tritium than the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, that contributes to the slow detritiation process.

The hydroxyl groups (OH) on the surface of the catalyst substrates (Kieselghur or Al<sub>2</sub>O<sub>3</sub>) could be a possible source of tritium surface contamination as they can retain tritium as (OT) by isotopic exchange with gas-phase tritium, with the total exchange capacity being determined by the T/H ratio in the gas, at equilibrium. Since the total surface area available in both catalysts were similar (~100 m<sup>2</sup>/g), it is possible that the differences in the observed contamination levels are related to differences in the surface densities of OH-groups on the two supports, at the operating temperature.

#### 4.4 Effect of Tritium-Surface Contamination

The detritiation process in the slow-detritiation region is significantly different for the two catalysts Pt/Al<sub>2</sub>O<sub>3</sub> and Ni/Kieselghur. These differences appear to be related to the differences in the tritium adsorption capacities of the catalysts at the operating temperature. Several experiments were carried out to determine the extent of tritium-surface contamination on these catalysts. In these tests, the tritium retained by the system components after a typical HITEX run at high tritium activities (695 Ci/m<sup>3</sup>) was determined for the two catalysts under comparable conditions. The results are shown in Figures 13 and 14 for Pt/Al<sub>2</sub>O<sub>3</sub> and Ni/Kieselghur catalysts respectively.

Following a HITEX run at high activity, the tritium adsorbed on the internal surfaces of the tubes was degassed by circulating dry He in the loop while bypassing the reactor and the permeator. A tritium concentration of ~70 mCi/m<sup>3</sup> (~7 pA) was measured in the loop for both catalysts with He. The cold reactor was then opened to the circulating gas. The tritium concentration in the loop decreased as the catalyst adsorbed tritium from the gas phase. The decrease in the tritium concentration was found to be larger for the Ni/Kieselghur catalyst than for the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. After the tritium concentration was stabilized, the reactor was heated to the operating temperature (400°C). The measured tritium concentration in the loop decreased for the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst while it increased for the Ni/Kieselghur catalyst. The reason for the two different behavior is not clear. Opening the diffuser to the loop flow did not significantly changed the tritium concentration measured in the loop in both cases. Following this step, He was evacuated and the bypass loop was filled with a 50%H<sub>2</sub>/He gas mixture and circulated. No significant change in the IC measurements was observed at this stage. The tritium concentration in the loop, however, increased significantly (~280 mCi/m<sup>3</sup> (~30 pA) for Pt/Al<sub>2</sub>O<sub>3</sub> and ~2350 mCi/m<sup>3</sup> (~250 pA) for Ni/Kieselghur) when the heated reactor was valved in. Both catalysts appear to retain substantial amounts of tritium compared to the rest of the surfaces in the system. According to these data, tritium contamination of metal surfaces in tubes and the tank surfaces does not appear to be significant enough to play a major role in the slow-detritiation process. The significant release of tritium from the catalyst with the 50%H<sub>2</sub>/He gas mixture appears to suggest that the tritium retained by the catalysts is in a strongly-adsorbed form but can exchanged easily with protium. As suggested Section 4.3, these adsorption sites could be identified with the surface hydroxyl

hydroxyl groups on the catalyst substrate. The Ni/Kieselghur catalyst appears to retain significantly more tritium (~8 times more) indicating a significantly higher surface-hydroxyl-group density on this catalyst under the reactor operating conditions. The fact that a large amount of tritium can still be desorbed from the catalyst after a typical HITEX run suggests that tritium is desorbed very slowly. These data explain the very early transition from fast- to slow-detrification region observed with the Ni/Kieselghur catalyst (see Section 4.3) as well as the differences observed in the slow-detrification region.

Towards the end of a typical HITEX run, surface hydroxyl groups are depleted with tritium as the catalyst is swamped with protium. Consequently, at the beginning of a HITEX run one can expect a decrease in the gas-phase tritium concentration as the tritium-depleted catalyst surface acts as a sink for tritium. The occurrence of this phenomenon at the beginning of a HITEX run is clearly seen in Figure 15 for the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. In this run, after circulating the CQ<sub>4</sub>/H<sub>2</sub> gas mixture in the bypass loop (reactor and permeator bypassed) the heated reactor was opened to the circulating gas. The initial tritium concentration as measured by the IC dropped initially from ~101 Ci/m<sup>3</sup> to roughly 99.5 Ci/m<sup>3</sup> consistent with the reduction in the loop pressure as a result of the increase in the loop volume. After this initial drop, the tritium concentration in the loop continued to decrease slowly before stabilizing at ~88 Ci/m<sup>3</sup>. This decrease in the tritium concentration is consistent with the loss of tritium from the gas phase due to isotopic exchange with surface-OH groups on the catalyst. The initial loss of tritium from the gas phase to the surface-OH groups amounted to ~12% for the 120 g Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.

Tritium contamination studies appear to suggest that catalyst substrates such as Al<sub>2</sub>O<sub>3</sub> and Kieselghur retains significant amounts of tritium probably as tritiated OH groups on the surface that contributes to the slow-detrification step which is detrimental to the overall HITEX process. Therefore, to extend the fast-detrification region to high DF values and to reduce the tritium responsible for the slow-detrification step, an alternative catalyst with low-tritium retention characteristics must be found.

#### 4.5 Test of Catalysts with Low-Tritium-Retention Characteristics

Two alternative catalysts were considered as potential substitutes for the current standard Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. They are Pt/Silicalite with a low OH-group density and Pt-metal sponge. Only the Pt/Silicalite catalyst was tested in the 1995 program.

##### 4.5.1 Pt/Silicalite Catalyst

The catalyst used was in the form of a corrugated screen (1.5 mm deep corrugations) rolled into 22.2 mm diameter x 152.4 mm long module containing 11.26 g of catalyst (8.57% Pt/Silicalite).

The HITEX run conditions with the Pt/Silicalite catalyst are listed in Table 9.



Table 9 - HITEK Tests with Pt/Silicalite Catalyst - Run Conditions

Run#	Flow L/min (STP)	Tritium Activity (Ci/m <sup>3</sup> )	Gas Composition (%)				Comments	
			CQ <sub>4</sub>	He	H <sub>2</sub> O vapor	H <sub>2</sub>	k	
51	5	109.0	4	0	0	96	-	dew point in tank: ~ -24/-20°C
52	5	106.0	4	0	0	96	0.83	dew point in tank: ~ -27°C
53	5	108.0	4	0	1.1	94.9	0.80	dew point in tank: ~ +14°C
54	2	111.0	4	0	1.1	94.9	1.16	dew point in tank: ~ +6°C
55	2	119.0	50	0	1.1	48.9	0.62	dew point in tank: ~ +13°C
56	2	118.0	50	0	1.1	48.9	0.72	dew point in tank: ~ +14°C. pure H <sub>2</sub> side throttled to 500 torr
57*	5	120.0	9.4	14. 5	1.1	75	0.71	dew point in tank: ~ +10°C
58	2	120.0	9.4	14. 5	1.1	75	0.96	dew point in tank: ~ +13°C
59**	5	126.0	18.8	29	1.1	51.1	0.60	dew point in tank: ~ +11°C

\* - ITER Composition (1)

\*\* ITER Composition (2)

Figure 16 compares the results obtained with the Pt/Silicalite catalyst under dry (~-27°C dew point) and humid (~+14°C dew point) conditions with the 4% CQ<sub>4</sub>/H<sub>2</sub> gas. For comparison, the results obtained with the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst under dry conditions is also shown in the same figure.

Humidification of the gas (dew point: +14°C) led to a slight decrease in the initial detritiation rate and the final DF achieved compared to dry conditions. However, with the Pt/Silicalite catalyst, the design-target DF of  $1 \times 10^5$  could be achieved within practical processing times even under humid conditions

Despite the low mass of the Pt/Silicalite catalyst (11 g) used, the initial detritiation rates are close to the rate obtained with 120 g of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. These data suggest different rate controlling mechanisms for the two types of catalysts

With the Pt/Silicalite catalyst, the change over from fast to slow detritiation occurred at a DF of  $\sim 2 \times 10^4$  compared to  $\sim 5 \times 10^3$  for Pt/Al<sub>2</sub>O<sub>3</sub> indicating a lower contamination level

for the Pt/Silicalite catalyst. A similar decrease in tritium contamination was also observed with the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst when the amount of catalyst used was reduced to 25 g (see Figure 7).

Simple calculations suggest the possibility for carbon formation on surfaces at temperatures below 400°C at CQ<sub>4</sub> mole fractions greater than 0.7, from methane decomposition. In the HITEX batch process, the mole fraction of CQ<sub>4</sub> in the gas can exceed 0.7 at the outlet of the permeator with high CQ<sub>4</sub> gas mixtures and can lead to carbon deposition in the permeator. The tests with 50% CQ<sub>4</sub> in the gas (Run #55 and Run #56) were carried out to determine the presence of carbon formation in the permeator by CQ<sub>4</sub> decomposition at the operating conditions. In Run #55, conditions for CQ<sub>4</sub> decomposition at the permeator operating temperature were maintained (CQ<sub>4</sub> mole fraction in the gas at the permeator outlet was ~0.8 and permeator temperature was 425°C). In Run #56, the pure-H<sub>2</sub> side was maintained at 500 torr to limit H<sub>2</sub> permeation to keep the CQ<sub>4</sub> mole fraction well below 0.7 (CQ<sub>4</sub> mole fraction at the outlet was ~0.45). Following the tests, the loop-gas was analyzed for the CQ<sub>4</sub> content by gas chromatography. The gas chromatographic analyses showed no change in the gas compositions in both cases indicating absence of carbon formation under the operating conditions. The experimental results from Run#55 and Run#56 are shown in Figure 17. The results obtained with 30% and 70% CQ<sub>4</sub>/H<sub>2</sub> gas mixtures with the Pt/Al<sub>2</sub>O<sub>3</sub> (120 g) catalyst are also shown in the same figure for comparison.

Figure 18 shows the experimental results obtained with ITER relevant gas mixtures (Run#57 to Run#59). The detritiation rates are slower with ITER relevant gas mixtures as expected (low R). With the ITER Composition (1), under humid conditions (dew point 10°C) the design-target DF of  $1 \times 10^5$  was reached after ~160 minutes of operation at 5 L/min (STP). Consistent with model predictions, a further decrease in R (ITER Composition (2)), reduced the initial detritiation rate as well as the overall DF.

Table 9 shows the values of k for all Pt/Silicalite experimental runs. At 5 L/min (STP), the k values calculated were significantly below 1 at all compositions indicating that complete isotopic equilibrium was not reached in the reactor for all gas compositions investigated. At high impurity contents, the k values were found to be significantly lower than 1 indicating increasing difficulty in ensuring complete isotopic equilibrium at low R under the operating conditions.

#### 4.6 Two-Stage HITEX Process

The two-stage HITEX concept was studied briefly in 1995. The experimental conditions are listed in Table 10.

Under dry conditions (Run#60), a DF of ~7.8 was obtained in the single-pass front end. The single-pass DF was unaffected under humid conditions (DF= ~7.3). These values are consistent with the theoretical calculations based on complete isotopic equilibrium at the reactor outlet.

Figure 19 shows the cyclic operation of the batch HITEX process graphically. Figure 20 shows DF as a function of time for the batch-HITEX process under the two-stage conditions. These results are compared against a batch run performed before the installation of the two-stage loop in the same figure for comparison.

In Run#61, the dew point of gas in the single-pass section was found to be difficult to control at  $-14^{\circ}\text{C}$  as required, with the current system. The dew point varied in a cyclic manner (long cycle time) between  $-30^{\circ}\text{C}$  and  $5^{\circ}\text{C}$  during the run. The cause of this instability is currently being investigated. Because of poor dew point control in the single-pass section, the dew point of the gas in the batch loop also could not be controlled at  $8^{\circ}\text{C}$  as required. The dew point in the batch loop was  $\sim 16/18^{\circ}\text{C}$  during the run.

Table 10 - Two-Stage HITEX Process Conditions

Single-Pass (R = 19)						
Run	Tritium Activity ( $\text{Ci}/\text{m}^3$ )	Flow Rate (L/min) (STP)	Composition			
	Inlet/Outlet	To Reactor/Tank	$\text{H}_2$	$\text{CQ}_4$	He	$\text{H}_2\text{O}$ dew point
			%			
60	567/1074	0.462/0.031	95	2	3	$-62^{\circ}\text{C}$
61	570/11280	0.462/0.028	95	2	2.8	0.2% unstable dew point
Batch HITEX (R = 3)/160 min Cycle Time						
60	?	5	75	10	15	Tank1: $-26/-23^{\circ}\text{C}$ Tank2: $-37/-24^{\circ}\text{C}$
61	?	5	73.9	10	15	1.1% Tank1: $16/18^{\circ}\text{C}$

With the two-stage system, the batch-HITEX performance was poor under both dry and humid conditions in the loop compared to the batch-HITEX performance achieved before the installation of the two-stage loop. With the two-stage loop, the transition from fast to slow detritiation occurred at a lower DF ( $\sim 1 \times 10^3$ ) for both dry and humid runs compared to a DF of  $\sim 1 \times 10^4$  for the humid run performed before the installation of the two-stage loop. Since the same components were used in the batch loop before and after the installation of the two-stage loop, these data appear to suggest the presence of dead-volumes in the batch loop in the two-stage system. This was confirmed in subsequent experiments carried out with the old-batch-loop configuration. These results show the need to reduce the dead-volumes and sources of contamination in the loop to obtain high ultimate DFs.

#### 4.7 Permeator Performance

The permeator performance characteristics was tracked over the course of the HITEX runs that extended for a 1.5 years. During this period, the RSD-50 permeator was operated for a total time of approximately 400 h. Figure 21 shows the permeator H<sub>2</sub> recovery fraction as a function of the run number under different operating conditions. The permeator recovery fraction remained constant (80-90%) under typical operating conditions and throughputs used in the HITEX tests. However, the permeate or pure H<sub>2</sub>-side pressure shows a definite increase with time indicating a gradual loss in the pumping speed of the bellows pump. As the figure shows, the average permeator recovery fraction remained relatively constant despite an increase in the pure-H<sub>2</sub> side pressure (100 to 200 torr) or changes in the H<sub>2</sub> pressure in the permeate side, throughput or gas composition. This is probably due to the fact that the permeator is oversized for the current HITEX requirements.

### 5. CONCLUSIONS AND RECOMMENDATIONS

In 1995, the HITEX test program focused on further testing and optimization of the basic HITEX concept, and construction and commissioning of a 2-stage HITEX system.

With respect to the HITEX process, the conclusions are as follows:

- detritiation by isotope swamping continues to provide reproducible results relative to the 1994 results with no deterioration over time;
- $DF > 10^4$  are achieved quickly under wet or dry conditions using the optimized batch HITEX process, as required for the ITER design;
- tests have been carried out with mixtures of CQ<sub>4</sub>, H<sub>2</sub>O, He, CO/ CO<sub>2</sub> and Q<sub>2</sub>, with no unexpected effects observed;
- achieving high DF with moist feed (or with oxygen containing feeds that can form moisture in the HITEX reactor) requires attention to the design to avoid water condensation in the loop, with the lines just after the permeator being the most important location. For example, trace heating of these lines should be used.
- three HITEX catalysts have been tested, the preference is as follows: 1) AECL Pt/Silicalite structured; 2) Johnson-Mathey Pt/Al<sub>2</sub>O<sub>3</sub>, 3) FzK Ni/SiO<sub>2</sub>. All catalysts are capable of catalyzing the isotope exchange reaction at around 400oC, but the silicalite catalyst showed the best behavior with moist feed gases, presumably because it has the most hydrophobic substrate.
- the catalyst has probably not been efficiently used in tests to date;

With respect to the 2-stage system, the 2-stage loop was designed, built and commissioned in 1995. First tests achieved a  $DF \sim 7$  in the first once-through HITEX stage, and  $DF \sim 10^4$  after 80 minutes in the second batch HITEX stage.

Future work, should include the following:

- continue tests on the HITEX system, including further work on catalyst optimization (both optimizing amount and geometry, as well as testing Pt sponge to minimize moisture holdup);
- improve the 2-stage HITEX loop to avoid dead legs and provide automatic operation, and operate for a variety of ITER-relevant feed conditions;
- improve the modeling of the HITEX system and update the ITER HITEX-based design;
- design HITEX components for high-tritium service.

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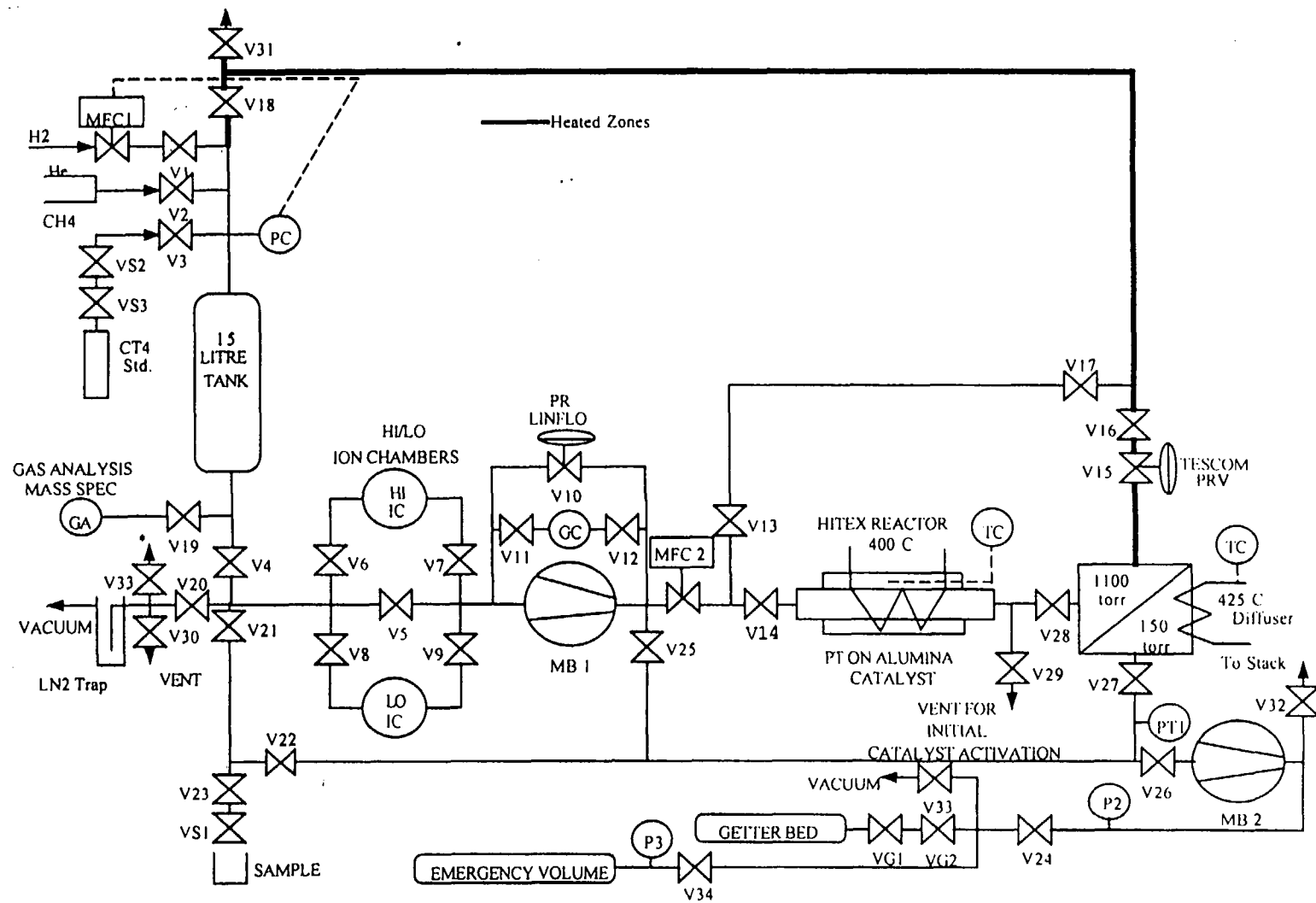


Figure 1. Batch HITEX experimental setup.

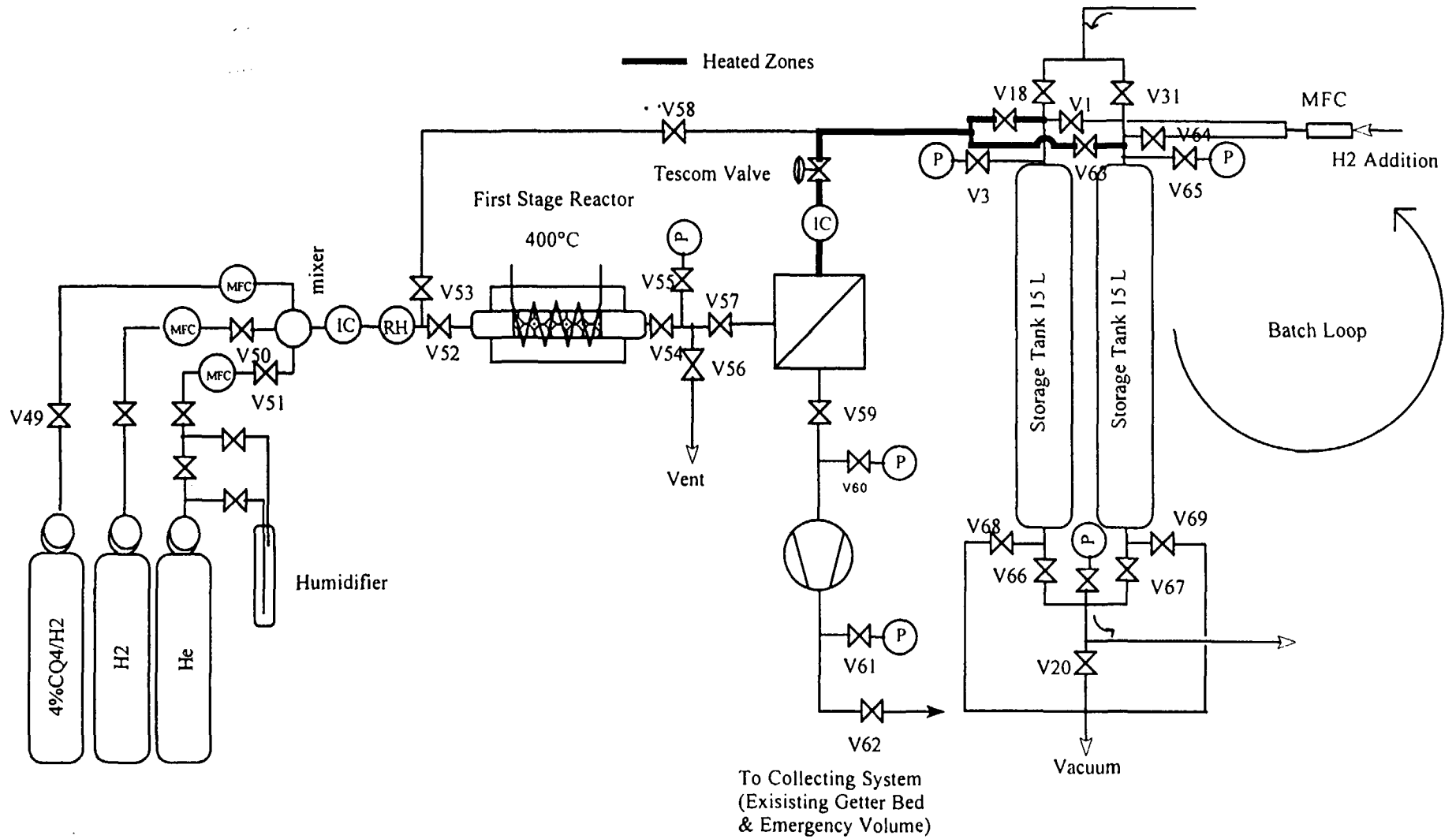


Figure 2. Two-stage HITEX experimental setup.

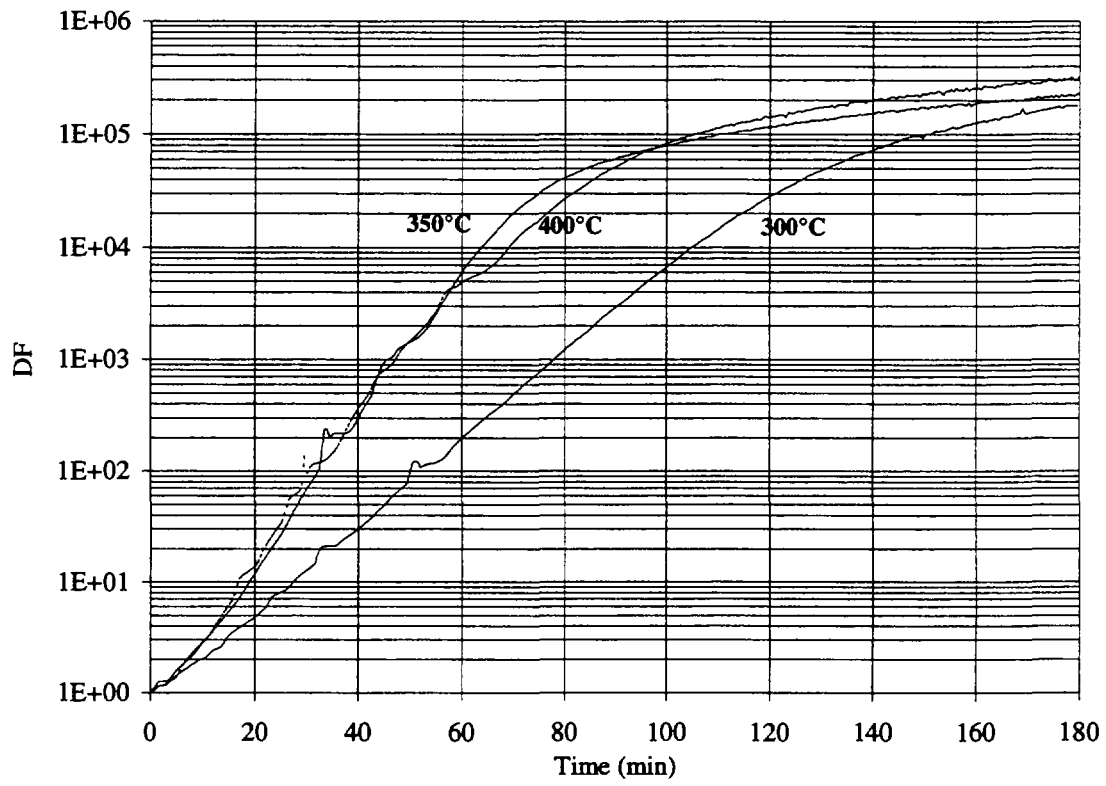


Figure 3. Effect of temperature.



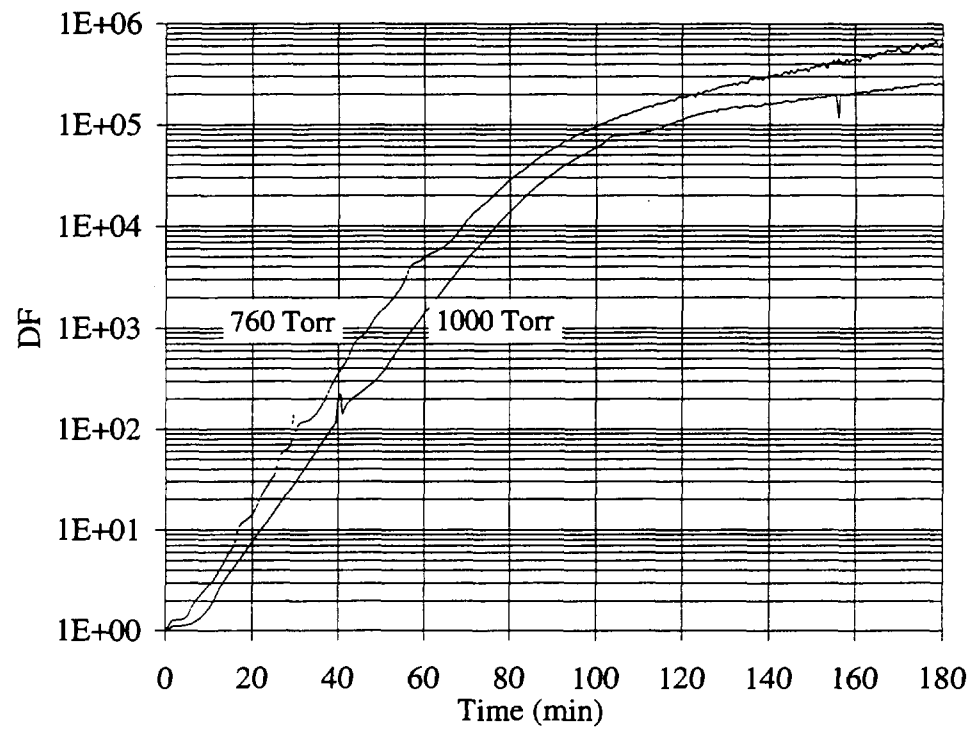


Figure 4. Effect of loop pressure.

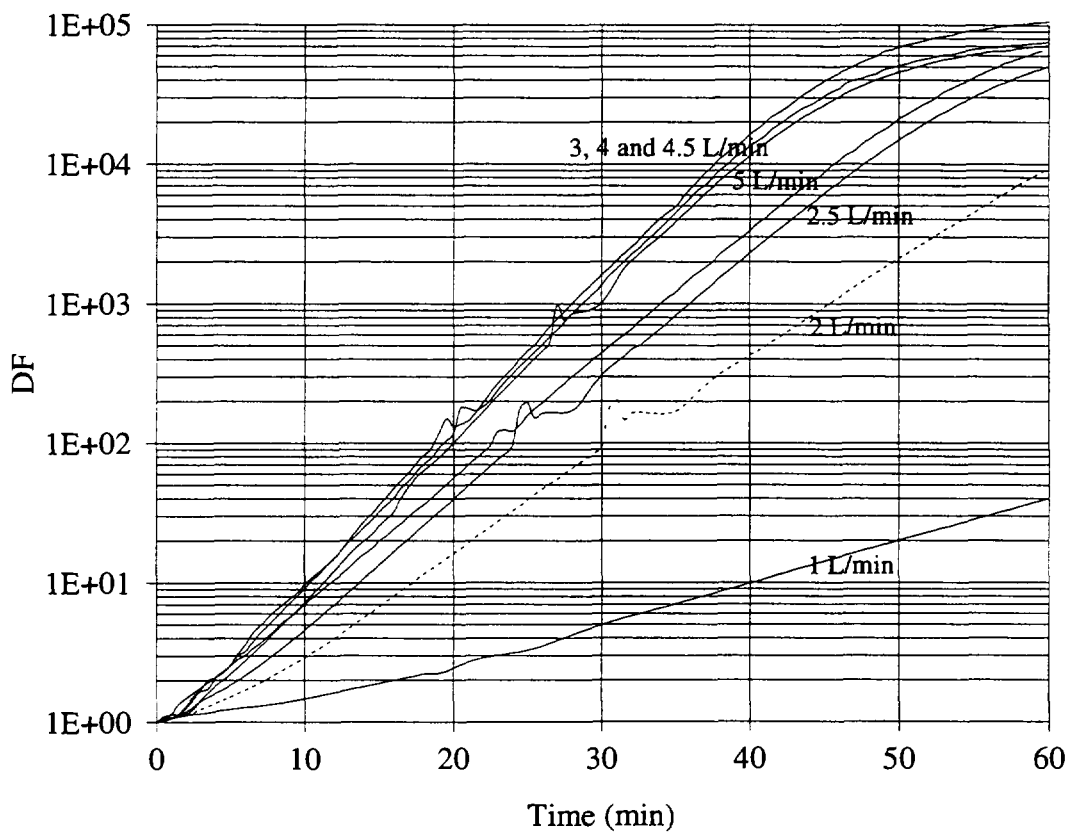


Figure 5. Effect of gas flow rate (21 g Pt/Al<sub>2</sub>O<sub>3</sub> catalyst).

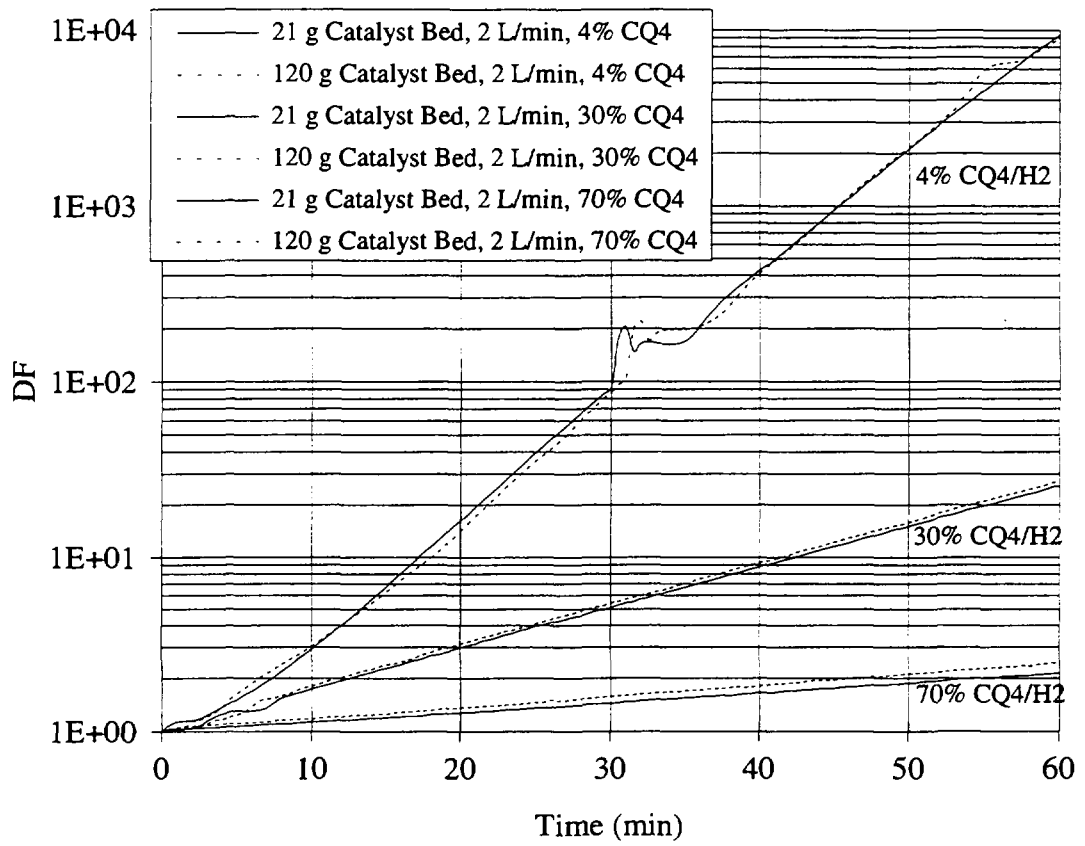


Figure 6. Effect of CQ<sub>4</sub> content and gas residence time (Pt/Al<sub>2</sub>O<sub>3</sub> catalyst).

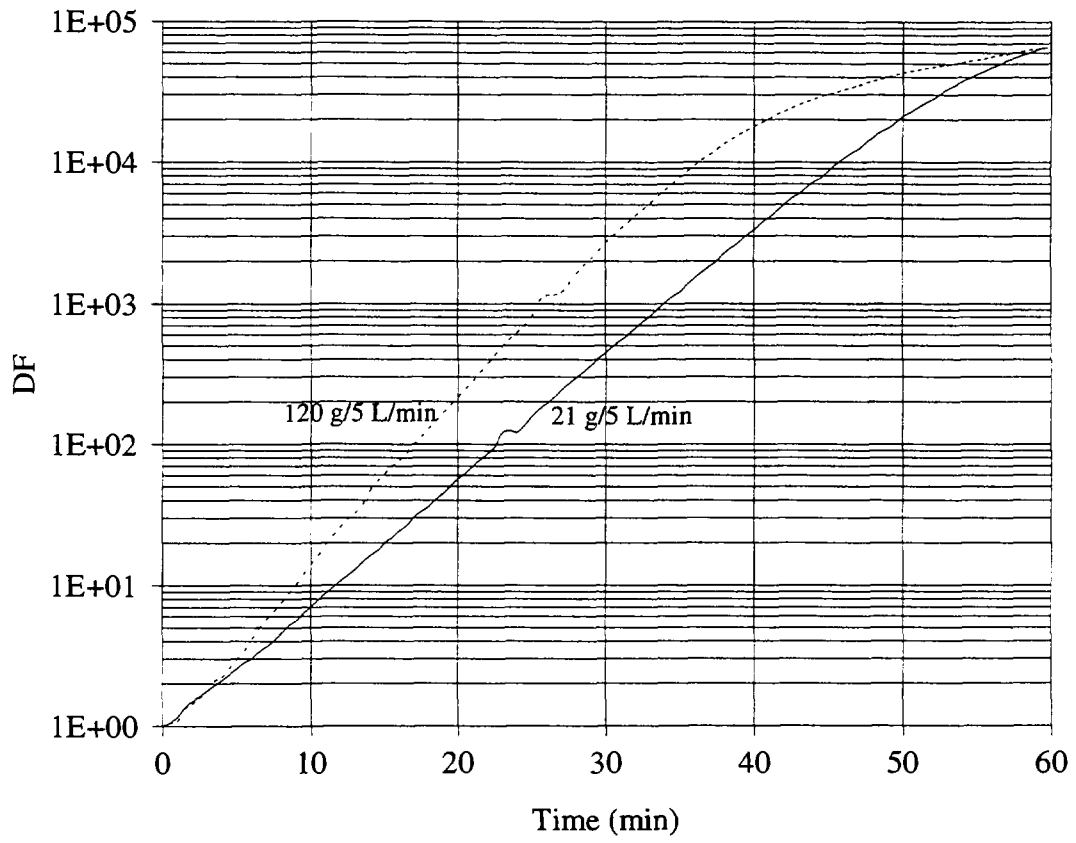


Figure 7. Effect of different amounts of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst (4% CQ<sub>4</sub>/Q<sub>2</sub> feed).

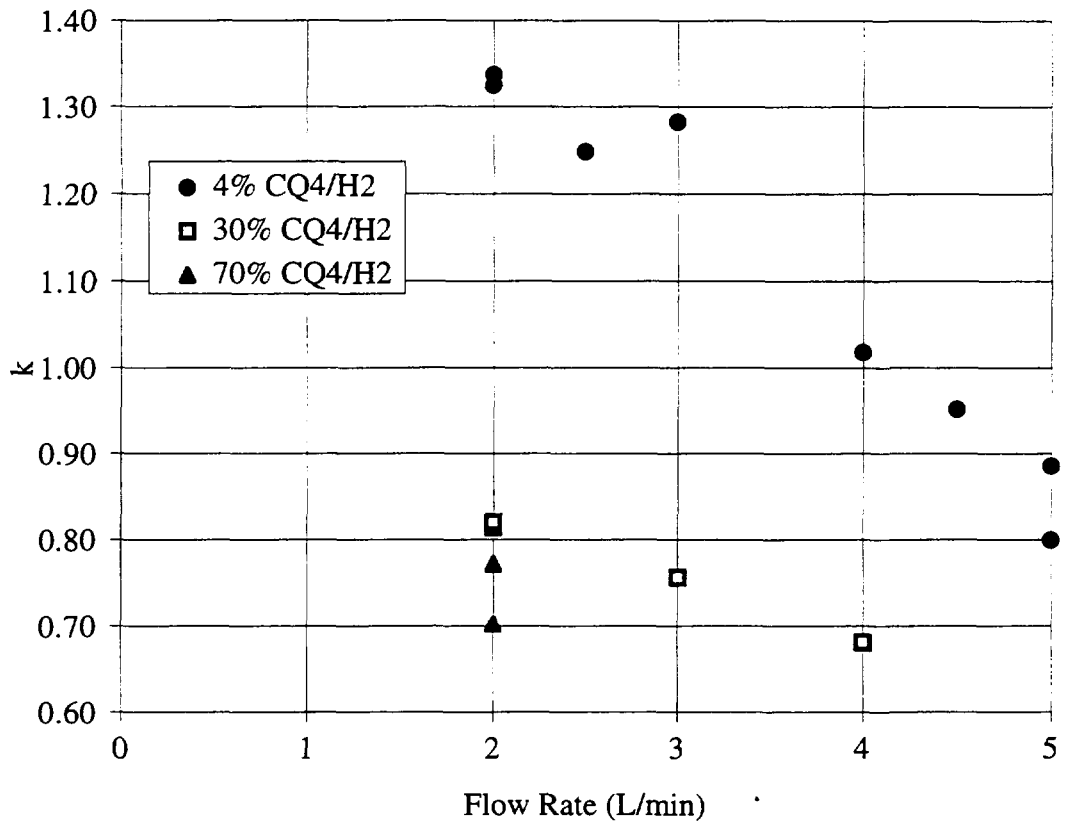


Figure 8. Effect of flow rate on k.

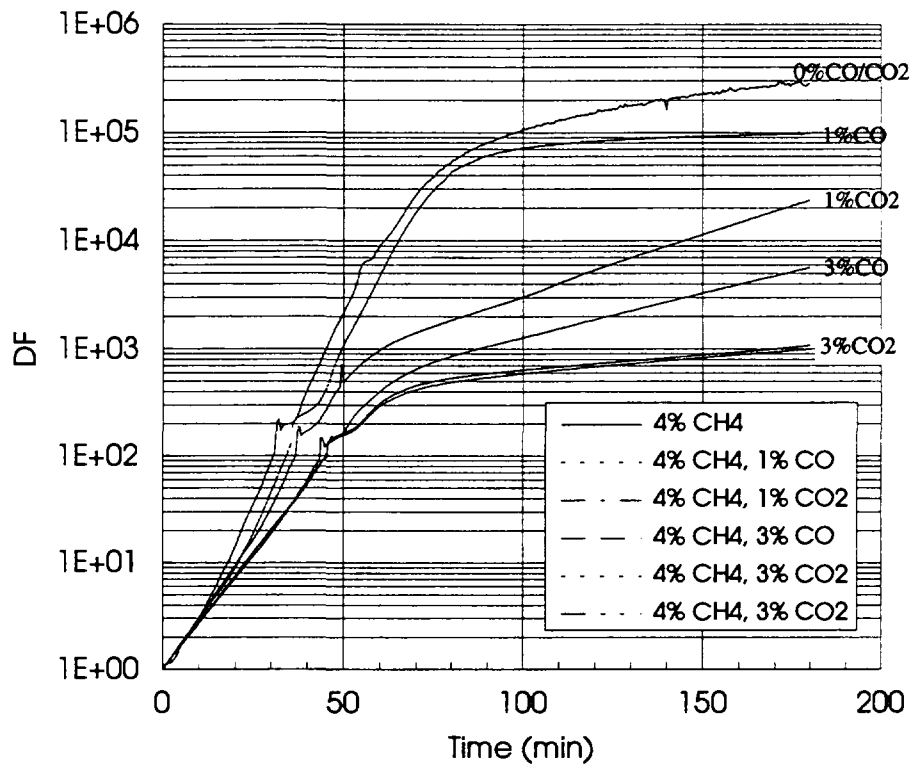


Figure 9. Effect of CO and CO<sub>2</sub>.

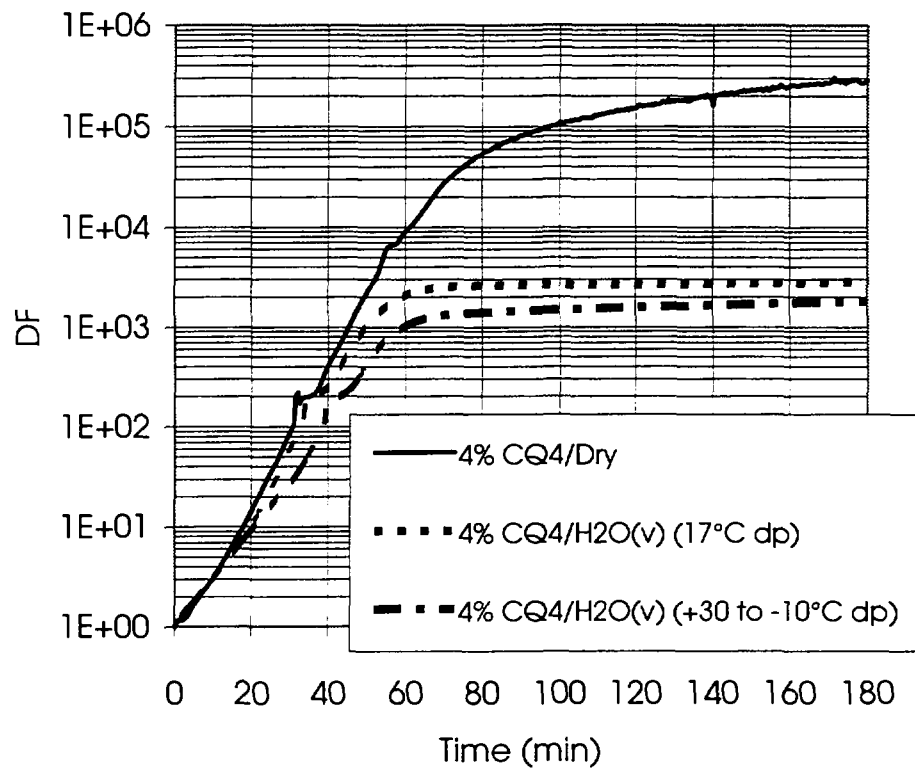


Figure 10. Effect of humidity (unheated loop).

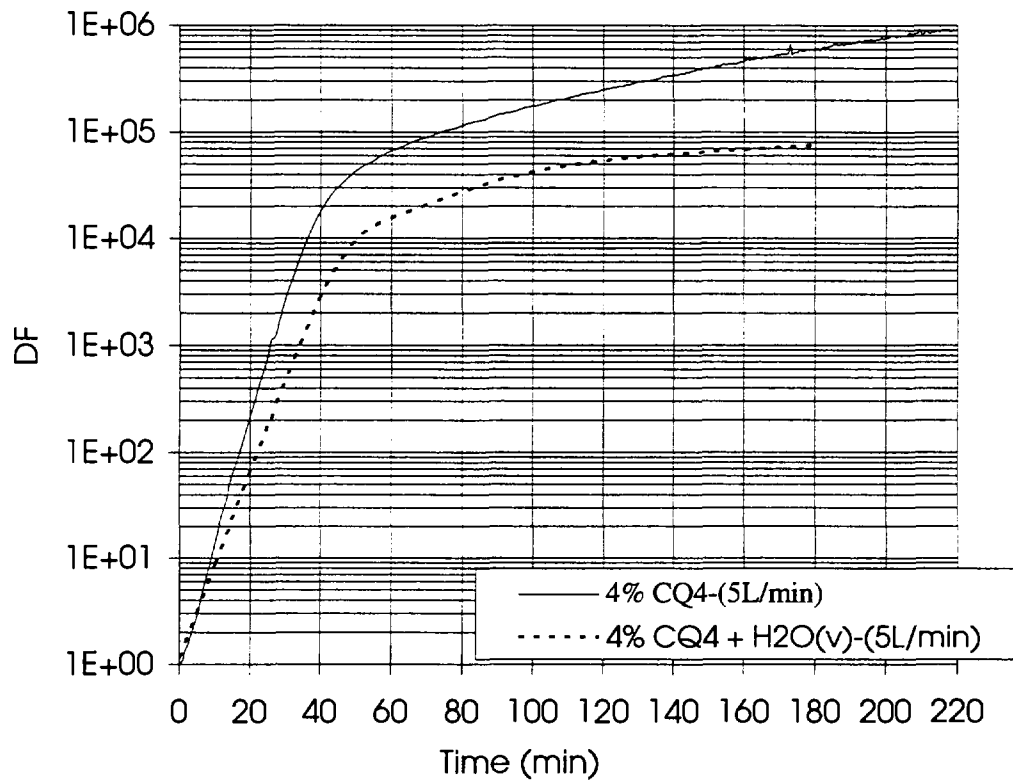


Figure 11. Effect of humidity (heated loop).



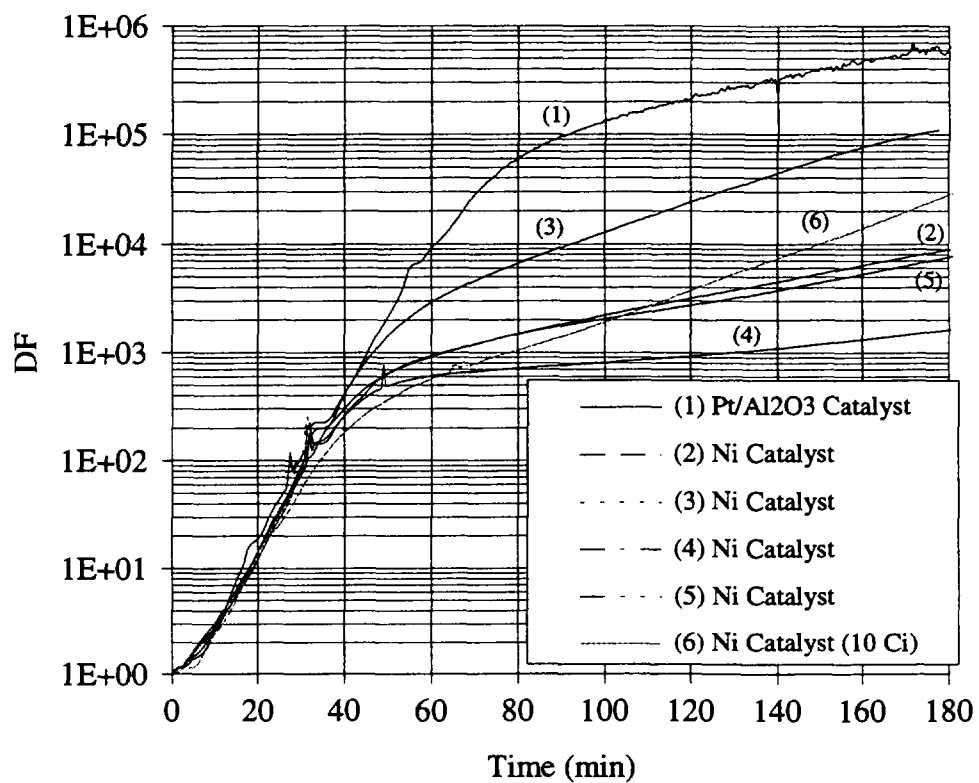


Figure 12. HITEX performance with Ni/Kieselguhr catalyst.

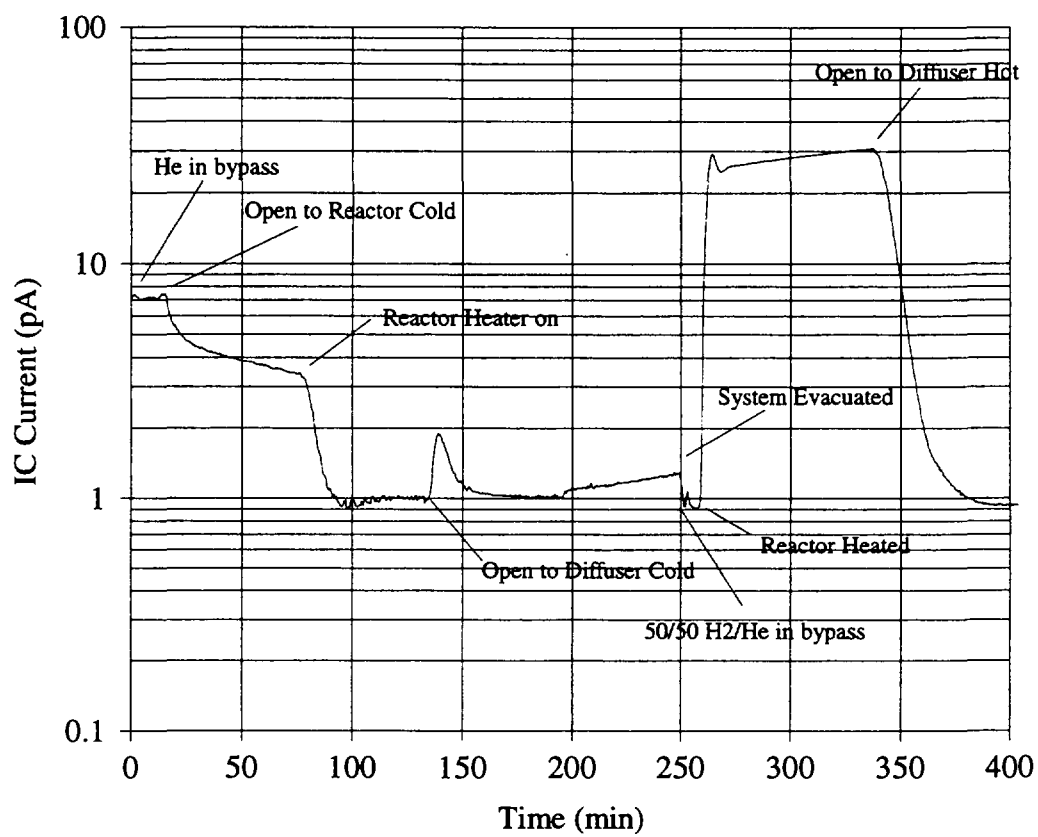


Figure 13. Loop contamination (Pt/Al<sub>2</sub>O<sub>3</sub> catalyst).

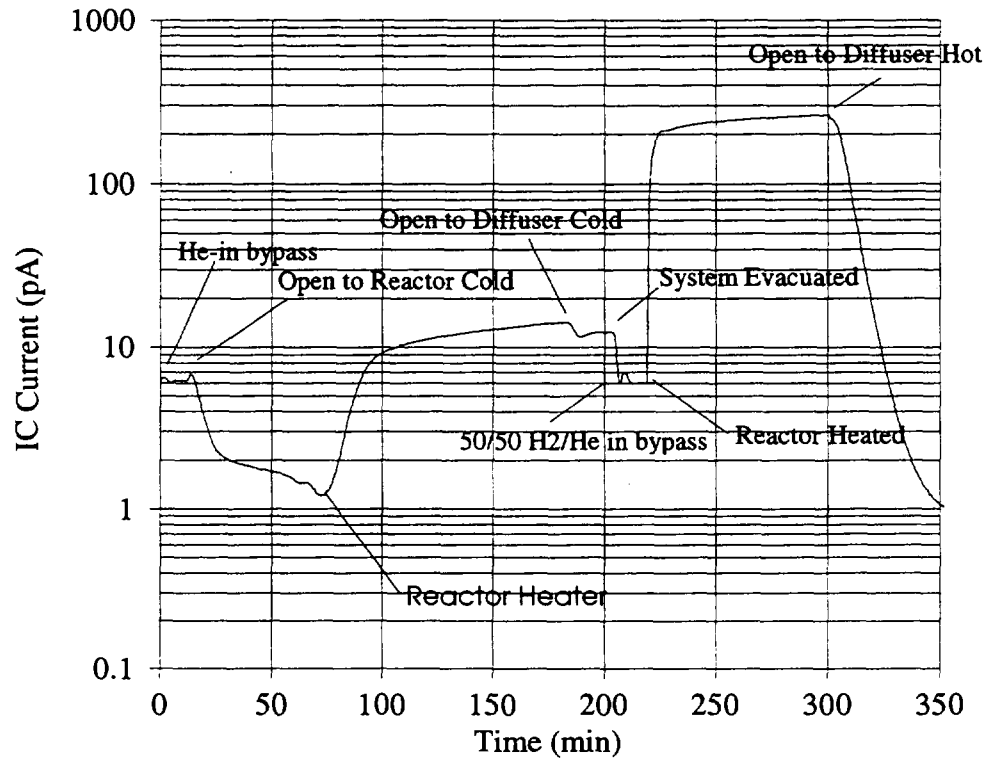


Figure 14. Loop contamination (Ni/Kieselghur catalyst).

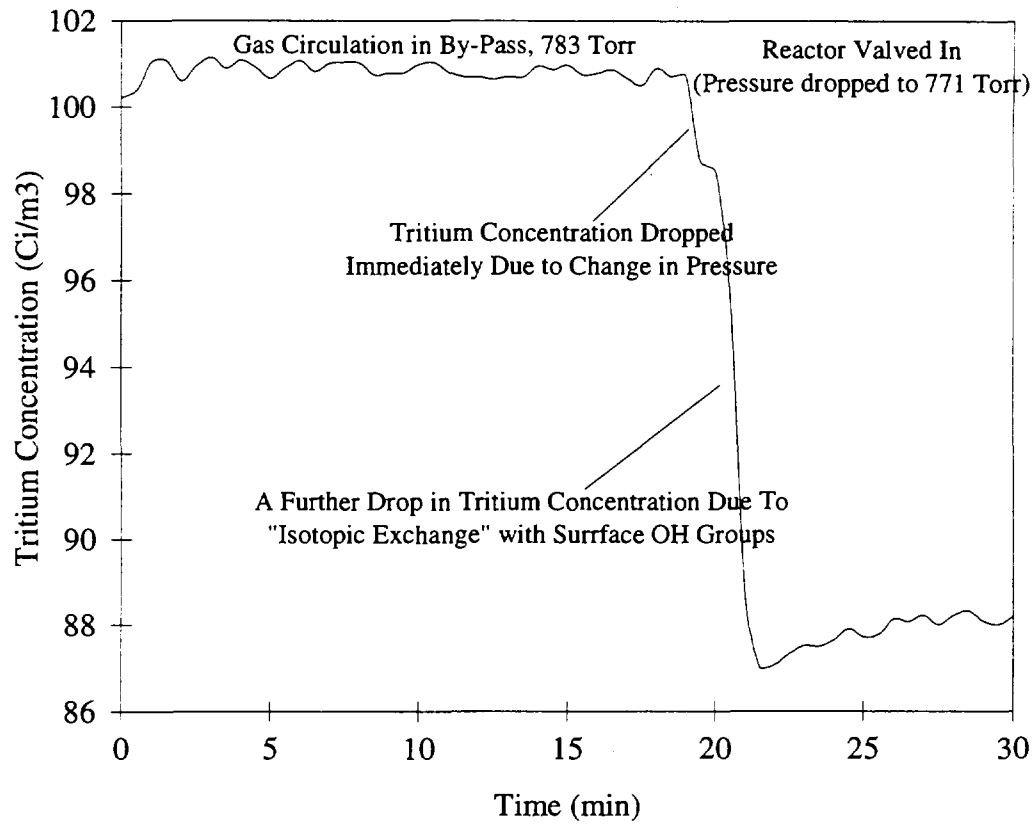


Figure 15. Tritium retention characteristics of the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.

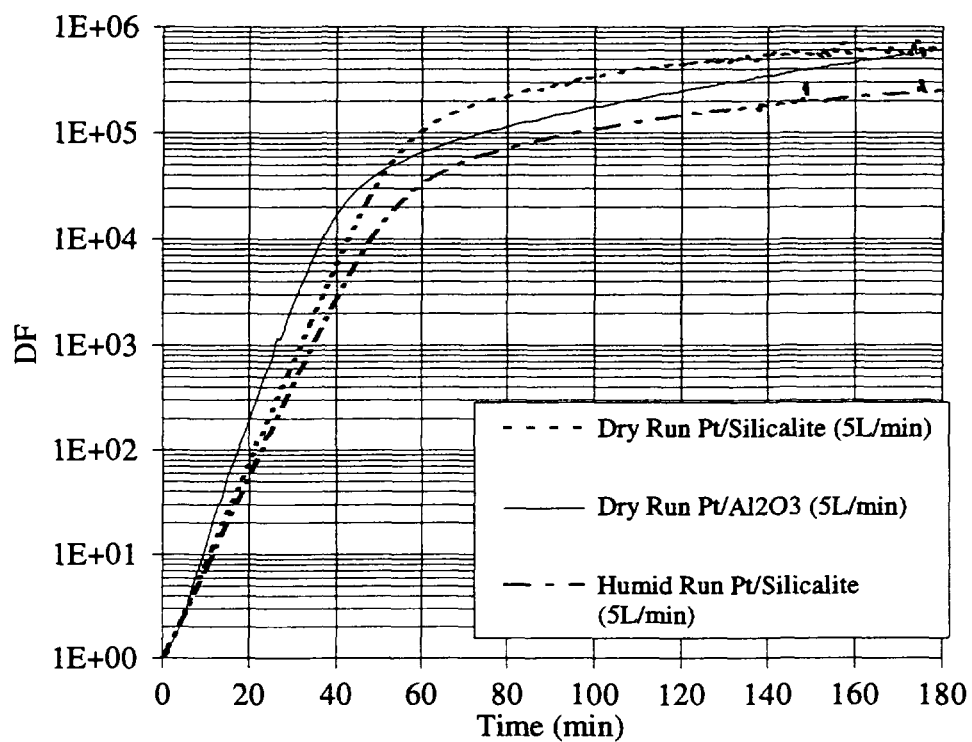


Figure 16. HITEX performance with the Pt/Silicalite catalyst.

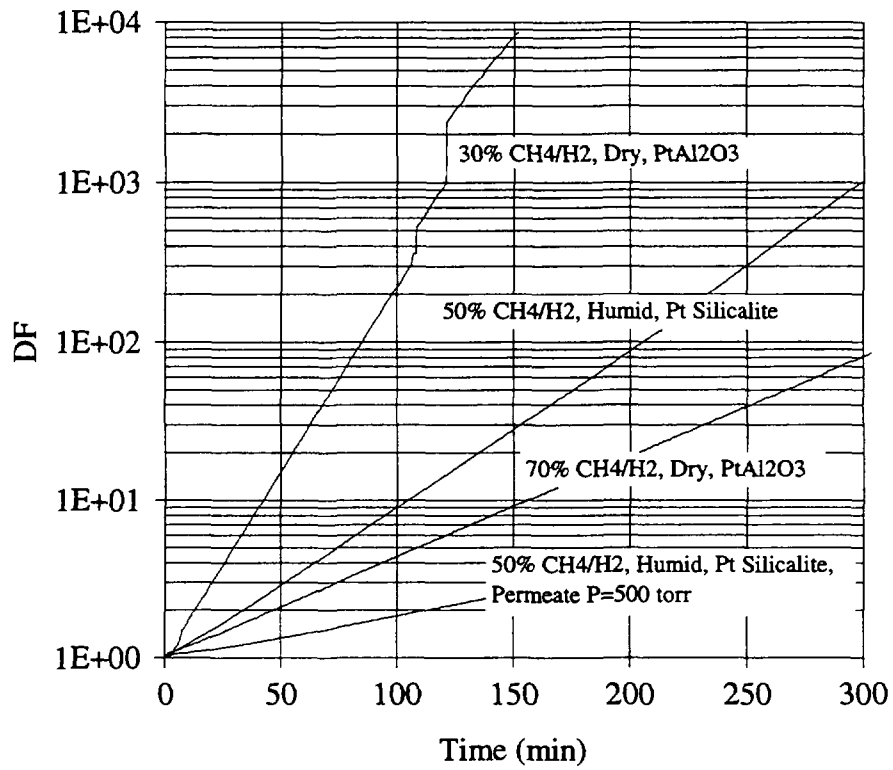


Figure 17. Effect of CQ<sub>4</sub> on HITEX performance with Pt/silicalite (2 L/min), Pt/Al<sub>2</sub>O<sub>3</sub> results shown for comparison. .

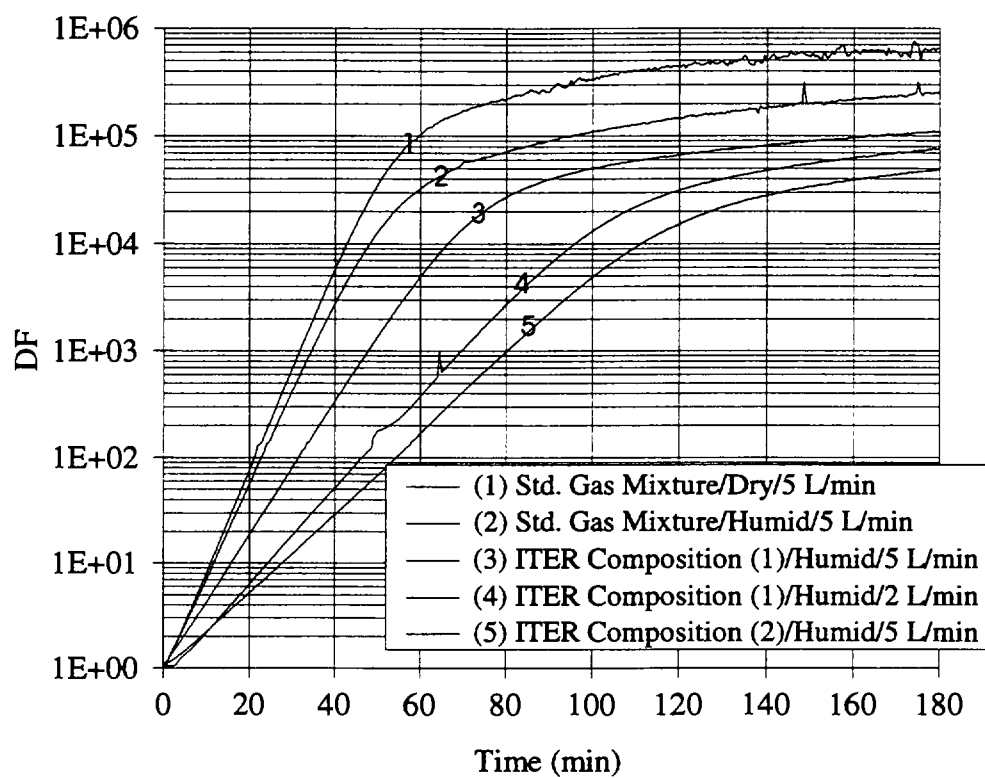


Figure 18. Summary of HITEX performance with Pt/Silicalite catalyst, showing effects of composition and flow rate.

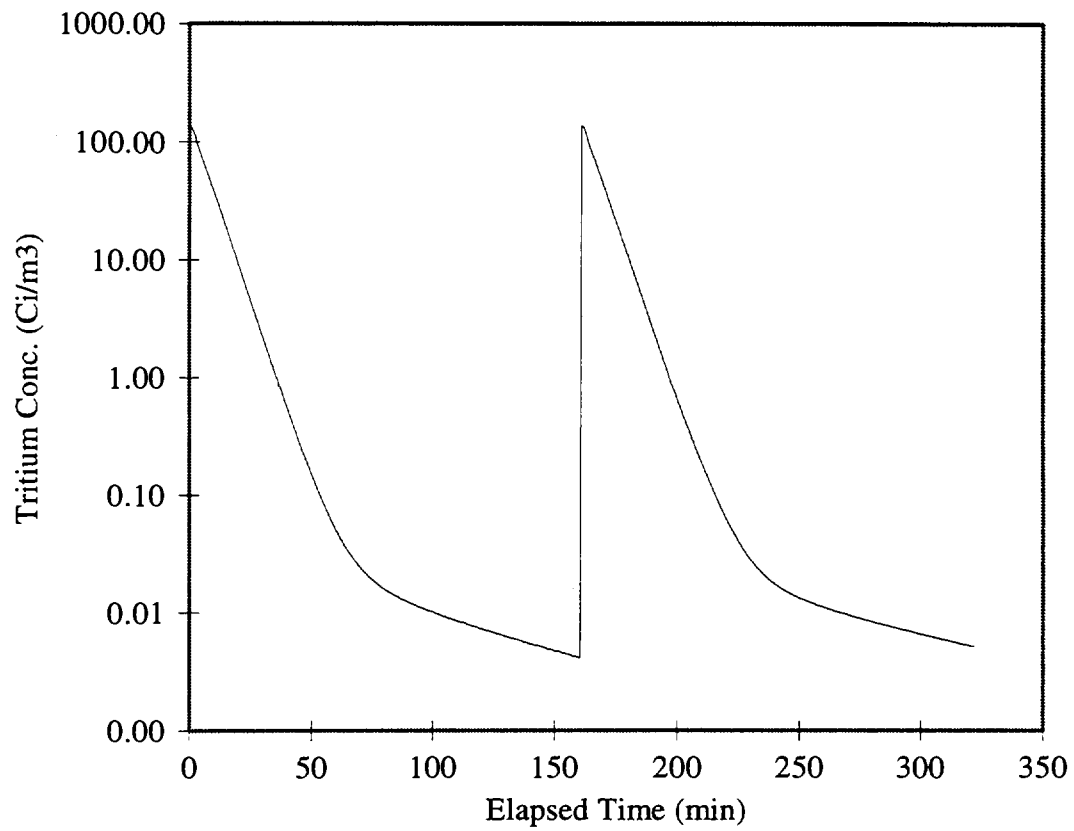


Figure 19. Two-stage HITEX loop performance (batch tank position).



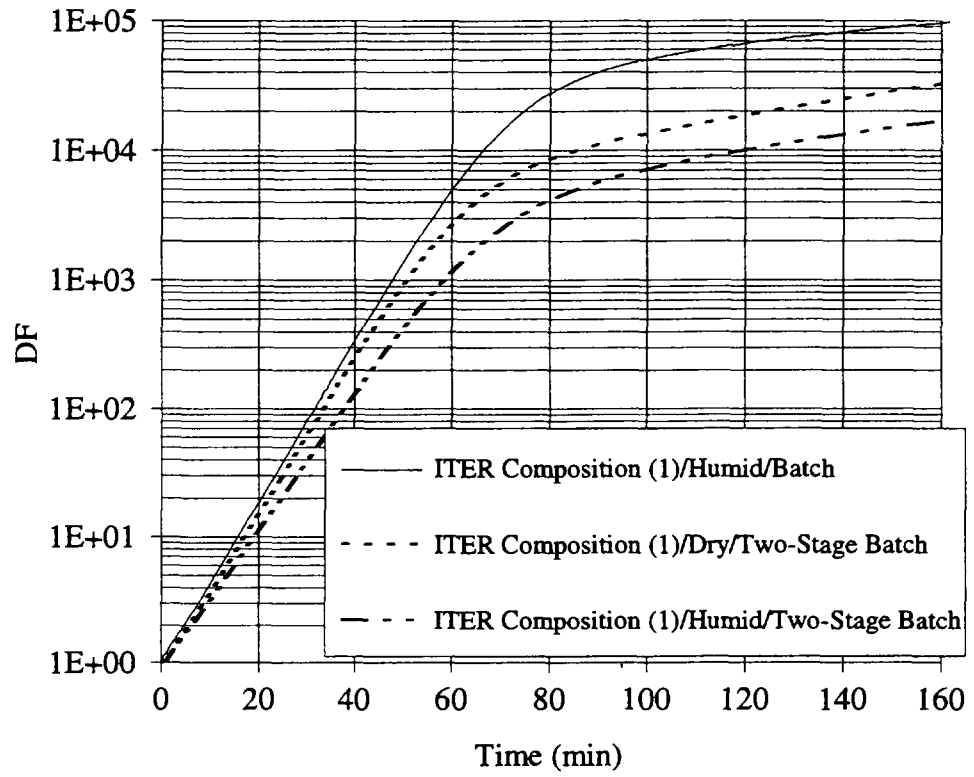


Figure 20. Two-stage HITEX loop performance (batch stage only).

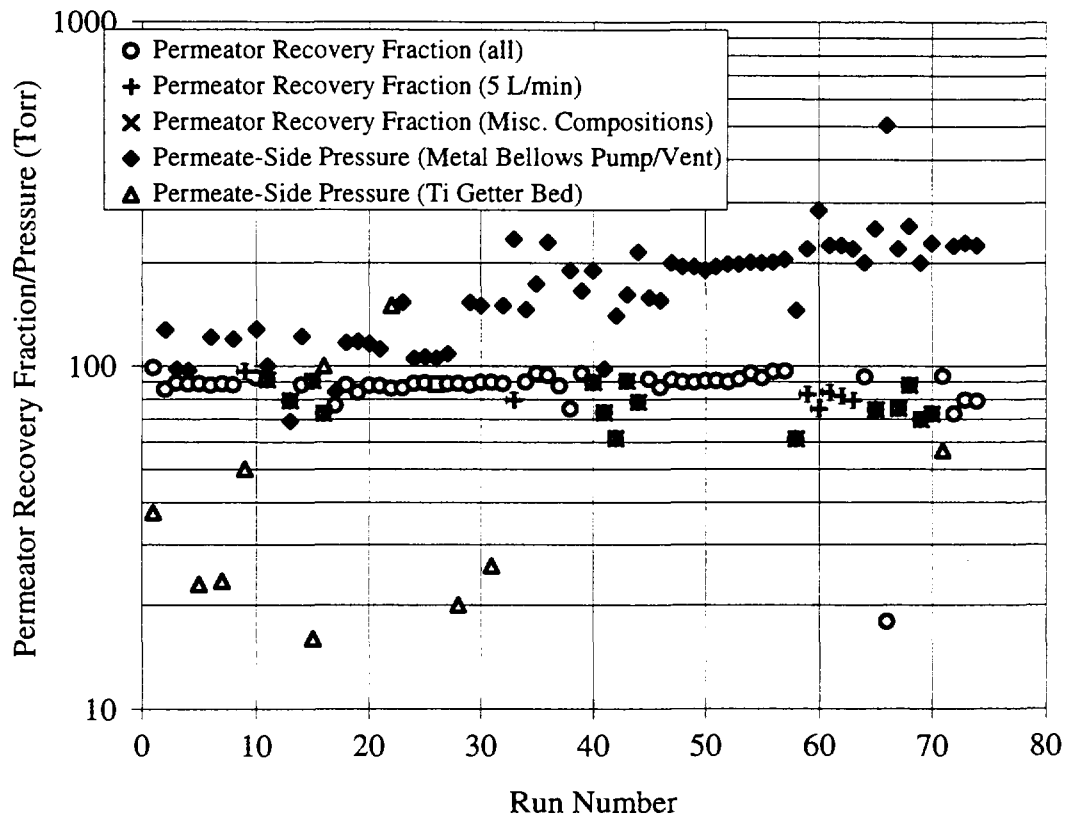


Figure 21. Long term permeator performance.