(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 February 2009 (12.02.2009)

PCT

(10) International Publication Number
WO 2009/021154 A2

(51) International Patent Classification:
C07C 17/04 (2006.01) *B01J 21/18* (2006.01)
C07C 21/06 (2006.01) *B01J 35/06* (2006.01)

(21) International Application Number: PCT/US2008/072549

(22) International Filing Date: 8 August 2008 (08.08.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/963,913 8 August 2007 (08.08.2007) US
12/187,887 7 August 2008 (07.08.2008) US

(71) Applicant *(for all designated States except US)*: **HONEYWELL INTERNATIONAL INC.** [US/US]; Law Department AB/2B, 101 Columbia Road, Morristown, NJ 07962 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **WANG, Haiyou** [US/US]; 811 Campbell Blvd, Amherst, New York 14228 (US). **TUNG, Hsueh Sung** [US/US]; 16 Vassar Drive, Getzville, New York 14068 (US).

(74) Agent: **BEATUS, Carrie**; Honeywell International Inc., Law Department AB/2B, 101 Columbia Road, Morristown, New Jersey 07962 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

(54) Title: DEHYDROCHLORINATION OF HYDROCHLOROFLUOROCARBONS USING PRE-TREATED ACTIVATED CARBON CATALYSTS

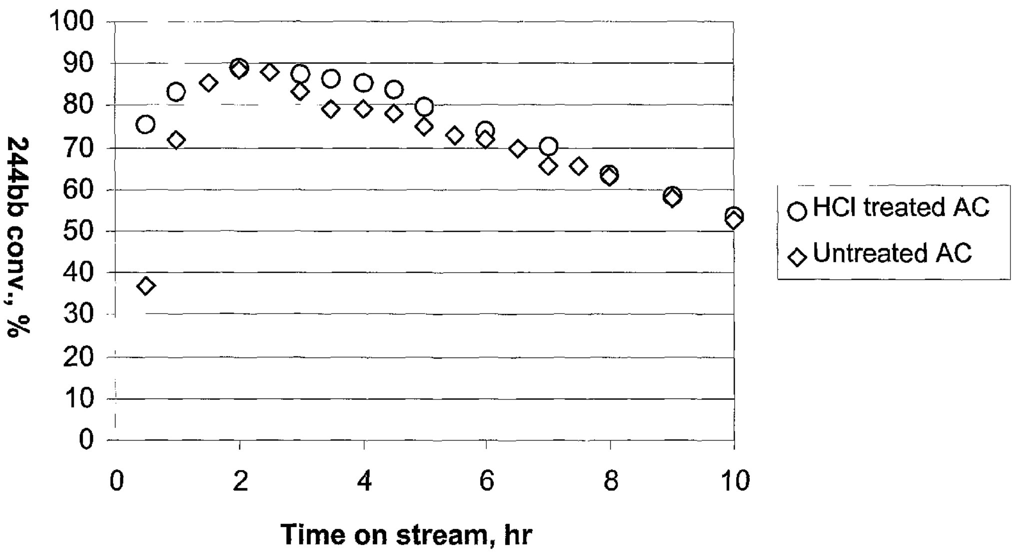

Fig. 1

(57) Abstract: The present disclosure provides methods for pre-treating activated carbon before it is used in a dehydrochlorination process. The methods can comprise mixing the activated carbon with an acid, an oxidizing agent in a liquid phase, or an oxidizing agent in a gas phase. Activated carbons undergoing one or more of these methods can exhibit improved stability during the dehydrochlorination process.

WO 2009/021154 A2

DEHYDROCHLORINATION OF HYDROCHLOROFLUOROCARBONS USING PRE-TREATED ACTIVATED CARBON CATALYSTS

CROSS REFERENCE TO RELATED APPLICATION

This application is related to, and claims priority to, U.S. Application No. 60/963,913, filed August 8, 2007 which is incorporated herein by reference.

BACKGROUND

1. Field of the Disclosure

The present disclosure relates to a method for using activated carbons in dehydrochlorination processes. More specifically, the present disclosure relates to a method for preparing hydroflouoroalkenes from hydrochlorofluoroalkanes using pretreated activated carbon.

2. Description of the Related Art

Activated carbons can be used as a catalyst for the dehydrochlorination, or conversion of hydrochlorofluorocarbons (HCFCs) into fluorinated alkenes that have lower global-warming potentials (GWP). These fluorinated alkenes can be used in a wide variety of applications, including as refrigerants, propellants, cleaning agents, and as monomers of macromolecule compounds.

The activated carbon tends to become deactivated quickly, however, which results in a drastically reduced rate of conversion of the HCFCs. Thus, there is a need for a method or process to improve the stability of activated carbon during the dehydrochlorination process.

SUMMARY OF THE INVENTION

Applicants have found demineralizing and/or oxidizing an activated carbon catalyst unexpectedly stabilizes the catalysts during certain dehydrochlorination reactions, for example, dehydrochlorinating 1,1,1,2-tetrafluoro-2-chloropropane (HCFC 244bb) to form 2,3,3,3-tetrafluoropropene (HFC-1234yf).

Accordingly, in certain aspects of the invention provided is a method for producing a fluorinated alkene comprising dehydrochlorinating a hydrofluorochloroalkane in the presence of a stabilized catalyst, wherein said stabilized catalyst is selected from the group consisting of demineralized activated carbon, oxidized activated carbon, or a combination thereof.

In another aspect of the invention, provided is a method for pre-treating an activated carbon catalyst comprising demineralizing said activated carbon catalyst and oxidizing said activated carbon catalyst.

In yet another aspect of the invention, provided is an activated carbon catalyst prepared according to such a pre-treatment process.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1-5 show experimental data concerning several embodiments of the method of the present disclosure.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

The present disclosure has advantageously discovered a novel method for improving the stability of activated carbon (AC) during the dehydrochlorination of HCFCs having at least one hydrogen and at least one chlorine on adjacent carbons. The AC can be pre-treated before being utilized in the dehydrochlorination process according to the methods discussed in greater detail below. As is shown in the provided data, this pre-treatment provides a substantial improvement in the stability and performance of the AC.

In a first embodiment, the AC is pre-treated with an acid at room temperature or higher. Preferred acids for this process include hydrochloric acid (HCl), hydrofluoric acid (HF), or a combination of the two. The pre-treatment with the acid comprises the following steps: 1) the AC is mixed with an aqueous solution of the acid, 2) the suspension is stirred for at least a first period of time at room temperature or higher and then filtered to separate the acid from the AC, 3) the AC is washed with distilled water until substantially free of ions from the acid, and 4) the AC is dried for at least a second period of time at a first temperature. The AC sample can be dried in air at a temperature of about 50°C to about 120°C, or higher. The AC can also be dried in air at a temperature of about 100°C to about 110°C. The first period of time can be from about 0.5 hours to about 24 hours, or longer. The second period of time can also be from about 0.5 hour to about 24 hours, or longer.

In a second embodiment, the pre-treatment of the AC can be carried out using an oxidizing agent in a liquid phase. In this embodiment, the pre-treatment comprises the following steps: 1) the AC is mixed with an aqueous solution of the oxidizing agent; 2) the suspension is stirred for at least a third period of time at room temperature or higher and then filtered to separate the AC from the oxidizing agent, 3) the AC is dried for at least a fourth period of time at a second temperature, and then 4) heat-treated in an inert gas, such as nitrogen, for at least a fifth period of time and at a third temperature. The third and fourth periods of time can also be from about 0.5 hour to about 24 hours, or longer. In step 3), the AC can be dried at about 50°C to about 120°C, or higher. In step 4), the fifth period of time can be about from about 0.5 hour to about 4 hours, or longer. The third temperature can be from about 250°C to 750°C or higher. The third period of time can also be 1 hour, and the third temperature can also be about 400°C. For the liquid phase, non-limiting examples of the oxidizing agent include nitric acid (HNO_3) and hydrogen peroxide (H_2O_2) aqueous solutions, or combinations of the two.

In a third embodiment, the pre-treatment of the AC can be carried out using an oxidizing agent in a gas phase. In this embodiment, the pre-treatment comprises the following steps: 1) the AC is loaded into a reactor, 2) pure or diluted gaseous oxidizing agent is flowed through the reactor, and 3) at least a portion of the AC is oxidized for a sixth period of time at a fourth temperature. In step 2, the oxidizing agent can be diluted with an inert gas, such as nitrogen. The concentration of the oxidizing agent in this diluted mixture can be from about 1% to about 10%. In step 3), the sixth period of time can be from about 5 seconds to about 12 hours or longer, or alternatively, about 2 hours. The fourth temperature can be from about 250°C to about 750°C, or higher. The fourth temperature can also be about 450°C. Generally speaking, a longer period of time is needed for a lower temperature. During this oxidation step, oxygen-containing groups are formed on the surface of the AC, and a small fraction of the AC may be burned off at elevated temperatures due to deep oxidation. For the gas phase, non-limiting examples of the oxidizing agent include diatomic oxygen (O_2) and carbon dioxide (CO_2), or combinations of the two.

The AC can be pre-treated with any one of the above described pre-treatments singly, or can be treated with any combination of the three. For example, the AC can be pre-treated with HCl, followed by a second pre-treatment with HNO_3. In addition, although the above-described methods concern AC that is pre-treated before being used in a dehydrochlorination process, the present disclosure also contemplates treating spent or deactivated AC with these methods, to rejuvenate the AC. The deactivated AC can undergo the treatment methods described above, and then be used in a dehydrochlorination process once they have been rejuvenated.

There are a number of HCFCs that can be used in the dehydrochlorination process of the present disclosure. Table 1 below shows a list of possible HCFCs and the resulting fluorinated alkenes that are produced by the dehydrochlorination process.

Table 1

HCFC	Fluorinated alkenes
$CF_3CFClCH_3$ (244bb)	$CF_3CF=CH_2$ (1234yf)
CF_3CHFCH_2Cl (244eb)	$CF_3CF=CH_2$ (1234yf)
CF_3CH_2CHFCl (244fa)	$CF_3CH=CHF$ (trans/cis-1234ze)
$CF_3CHClCH_2F$ (244db)	$CF_3CH=CHF$ (trans/cis-1234ze)
$CF_3CFClCH_2F$ (235bb)	$CF_3CF=CHF$ (Z/E-1225ye)
$CF_3CHFCHFCl$ (235ea)	$CF_3CF=CHF$ (Z/E-1225ye)
$CF_3CH_2CF_2Cl$ (235fa)	$CF_3CH=CF_2$ (1225zc)
$CF_3CHClCHF_2$ (235da)	$CF_3CH=CF_2$ (1225zc)
$CF_3CFClCHF_2$ (226ba)	$CF_3CF=CF_2$ (1216)
CF_3CHFCF_2Cl (226ea)	$CF_3CF=CF_2$ (1216)

In any of the above-described embodiments, the HCFC that undergoes dehydrochlorination can be 1,1,1,2-tetrafluoro-2-chloropropane, also known as 244bb, and the resultant fluorinated alkene is 2,3,3,3-tetrafluoropropene, also known as 1234yf. The following experimental data demonstrates that pre-treatment of AC, before being used in the dehydrochlorination process, can improve the ability of the ACs to catalyze the conversion of HCFCs into fluorinated alkenes, over that which is achieved with untreated AC. Methods of dehydrochlorination are described in co-pending United States Patent Application No. 11/619,592, filed on January 3, 2007, (hereinafter "the '592 application") which is incorporated herein by reference. The AC is available from a number of sources, including the Alfa Aesar Corporation.

Example 1: 244bb dehydrochlorination over untreated and HCl-treated ACs

In Example 1, untreated and HCl-treated activated carbons (ACs) were used as dehydrochlorination catalysts. 20 cc of catalyst granules was used. A mixture of 92.7% of 244bb/6.5% of 1233xf was passed through a bed of each of the AC catalysts at a rate of 6 g/h. 1233xf is an intermediate product formed during the fluorination of $CCl_2=CClCH_2Cl$, and is used as raw material for producing 244bb, as described in the '592 application. For this reason, streams of 244bb often comprise some amount of 1233xf. The temperatures at the bottom of the catalyst bed and at the top of catalyst bed were recorded and reported. As shown in Figure 1, which shows data at 350-385°C, the stability of AC was slightly improved after treatment with HCl.

Example 2: 244bb dehydrochlorination over HCl- and HCl & HNO_3-treated activated carbons

In Example 2, AC pretreated with HCl, and AC pre-treated with both HCl & HNO_3, according to the methods described above, were used as dehydrochlorination catalysts. 20 cc of catalyst granules was used. A mixture of 92.7% of 244bb/ 6.5% of 1233xf was passed through a bed of each of the AC catalysts at a rate of 6 g/h. The temperatures at the bottom of the catalyst bed and at the top of catalyst bed were recorded and reported. As shown in Fig. 2, at 350-385°C, compared to the AC pre-treated with only HCl, the HCl & HNO_3 pre-treated AC showed much higher stability. Over the latter the conversion of 244bb was still above 80% after 10 hours on stream, while over the former it was already below 55% after 10 hours on stream. This result suggests oxidation treatment in liquid phase with HNO_3, particularly when used in conjunction with the pre-treatment of HCl, can greatly improve the stability of AC.

Example 3: 244bb dehydrochlorination over HCl- and HCl & H_2O_2-treated activated carbons

In Example 3, AC pre-treated with HCl, and AC pre-treated with both HCl & H_2O_2, according to the methods described above, were used as dehydrochlorination catalysts. 20 cc of catalyst granules was used. A mixture of 92.7% of 244bb/ 6.5% of 1233xf was passed through a bed of each of the AC catalysts at a rate of 6 g/h. The temperatures at the bottom of the catalyst bed and at the top of catalyst bed were recorded and reported. As shown in Fig. 3, at 350-385°C, compared to the AC pre-treated with HCl only, the AC pre-treated with both HCl & H_2O_2 exhibited higher stability. The latter exhibited a rate of conversion of 244bb of about 70% after 10 hours on stream, while the former exhibited a rate of below about 55% after 10 hours on stream. This result suggests that pre-treatment of the AC in liquid phase with H_2O_2, after pre-treatment with HCl, can improve the stability of the AC over that which is only pre-treated with HCl.

Example 4: 244bb dehydrochlorination over HCl- and HCl & 5% O_2/N_2-treated activated carbons

In Example 4, AC pre-treated with only HCl and AC pre-treated with HCl & a mixture of 5%O_2/95%N_2 were used as dehydrochlorination catalysts. 20 cc of catalyst granules was used. A mixture of 92.7% of 244bb/6.5% of 1233xf was passed through a bed of each of the AC catalysts at a rate of 6 g/h. The temperatures at the bottom of the catalyst bed and at the top of catalyst bed were recorded and reported. As shown in Fig. 4, at 350-385°C, the AC treated with HCl and the mixtures of 5% of O_2/95% of N_2 was able to maintain its activity at the level of about 70% for almost 7 hours (from the 3^{rd} to the 10^{th} hours on stream), at least. The performance of the HCl-treated AC, in contrast, decreased over time. This indicates that oxidation pre-treatment of the AC with a gaseous O_2 mixture, particularly in conjunction with pre-treatment with HCl, can greatly improve the stability of ACs long term.

Example 5: 244bb dehydrochlorination over pristine and HNO_3-treated activated carbons

In Example 5, untreated AC, and AC pre-treated with HNO_3 according to the method described above, were used as dehydrochlorination catalysts. 20 cc of catalyst granules was used in a typical run. A mixture of 97.2% of 244bb/2.0% of 1233xf was passed through catalyst bed at a rate of 6 g/h. The temperatures at the bottom of the catalyst bed and at the top of catalyst bed were recorded and reported. As shown in Figure 5, at 350-385°C, the AC pre-treated with HNO_3 was able to maintain its activity at the level of above 75% from the 4th to the 8^{th} hour. The performance of the untreated AC, by contrast, steadily decreased over time. This indicates that the stability of the AC can be significantly improved by pre-treatment with HNO_3, even without pre-treatment with HCl.

The present invention having been thus described with particular reference to the preferred forms thereof, it will be obvious that various changes and modifications may be made therein without departing from the spirit and scope of the present invention as defined in the appended claims.

CLAIMS

What is claimed is:

1. A method for producing a fluorinated alkene comprising:

dehydrochlorinating a hydrofluorochloroalkane in the presence of a stabilized catalyst, wherein said stabilized catalyst is selected from the group consisting of demineralized activated carbon, oxidized activated carbon, or a combination thereof.

2. The method of claim 1 wherein said hydrochlorofluoroalkane is selected from the group consisting of 1,1,1,2-tetrafluoro-2-chloropropane, 1,1,1,2-tetrafluoro-3-chloropropane, 1,1,1,3-tetrafluoro-3-chloropropane, 1,1,1,3-tetrafluoro-2-chloropropane, 1,1,1,2,3-pentafluoro-2-chloropropane, 1,1,1,2,3-pentafluoro-3-chloropropane, 1,1,1,3,3-pentafluoro-3-chloropropane, 1,1,1,3,3-pentafluoro-2-chloropropane, 1,1,1,2,3,3-hexafluoropropane-2-chloropropane, and 1,1,1,2,3,3-hexafluoro-3-chloropropane.

3. The method of claim 1 wherein said hydrochlorofluoroalkane is 1,1,1,2-tetrafluoro-2-chloropropane.

4. The method of claim 1 wherein said fluorinated alkene is selected from the group consisting of: 2,3,3,3-tetrafluoropropene, 1,3,3,3-tetrafluoropropene,

1,2,3,3,3-pentafluoropropene, 1,1,3,3,3-pentafluoropropene, and 1,1,2,3,3,3-hexafluoropropene.

5. The method of claim 3 wherein said fluorinated alkene is 2,3,3,3-tetrafluoropropene.

6. The method of claim 1 wherein said stabilized catalyst is activated carbon that has been demineralized in the presence of at least one acid selected from the group consisting of hydrochloric acid and hydrofluoric acid.

7. The method of claim 6 wherein said acid is hydrochloric acid.

8. The method of claim 1 wherein said stabilized catalyst is activated carbon that has been oxidized in the presence of at least one liquid phase oxidizing agent selected from the group consisting of nitric acid and hydrogen peroxide.

9. The method of claim 1 wherein said stabilized catalyst is activated carbon that has been oxidized in the presence of at least one vapor phase oxiziding agent selected from the group consisting of O_2 and CO_2.

10. The method of claim 6 wherein said activated carbon further has been oxidized in the presence of nitric acid.

11. The method of claim 6 wherein said activated carbon further has been oxidized in the presence of hydrogen peroxide.

12. The method of claim 6 wherein said activated carbon further has been oxidized in the presence of O_2.

13. The method of claim 1 wherein said stabilized catalyst is activated carbon that has been subjected to a demineralization process comprising the following:

forming a suspension comprising said activated carbon and at least one acid selected from the group consisting of hydrochloric acid and hydrofluoric acid;

stirring said suspension at a temperature of at least about 22 °C for a first period of time from about 0.5 to about 24 hours;

filtering said suspension, to separate said activated carbon catalyst from said acid;

washing said catalyst to remove substantially all free ions from said activated carbon catalyst; and

drying said catalyst at a temperature of at least about 50 °C for a second period of time from about 0.5 to about 24 hours.

14. The method of claim 1 wherein said stabilized catalyst is activated carbon that has been subjected to a liquid phase oxidation process comprising the following:

forming a suspension comprising said activated carbon and at least one oxidizing agent selected from the group consisting of nitric acid and hydrogen peroxide;

stirring said suspension at a temperature of at least about 22 °C for a first period of time from about 0.5 to about 24 hours;

filtering said suspension, subsequent to said stirring, to separate said activated carbon from said oxidizing agent;

drying said activated carbon, subsequent to said filtering, at a temperature of at least about 50 °C for a second period of time from about 0.5 to about 24 hours; and

heat-treating said catalyst in an inert gas for a third period of time from about 0.5 to about 4 hours at a temperature of about 250 °C to about 750 °C.

15. The method of claim 1 wherein said stabilized catalyst is activated carbon that has been subjected to a vapor phase oxidation process comprising the following:

contacting said activated carbon with said gaseous oxidizing agent at a temperature of about 250 to about 750 °C for a period of time from about 5 seconds to about 12 hours.

16. A method for pre-treating an activated carbon catalyst comprising:

demineralizing said activated carbon catalyst, and

oxidizing said activated carbon catalyst.

17. The method of claim 16 wherein said demineralizing involves contacting said activated carbon catalyst with at least one acid selected from the group consisting of hydrochloric acid and hydrofluoric acid.

18. The method of claim 16 wherein said oxidizing involves contacting said activated carbon catalyst with at least one oxidizing agent selected from the group consisting of nitric acid, hydrogen peroxide, O_2, and CO_2.

19. An activated carbon catalyst prepared according to the process of claim 16.

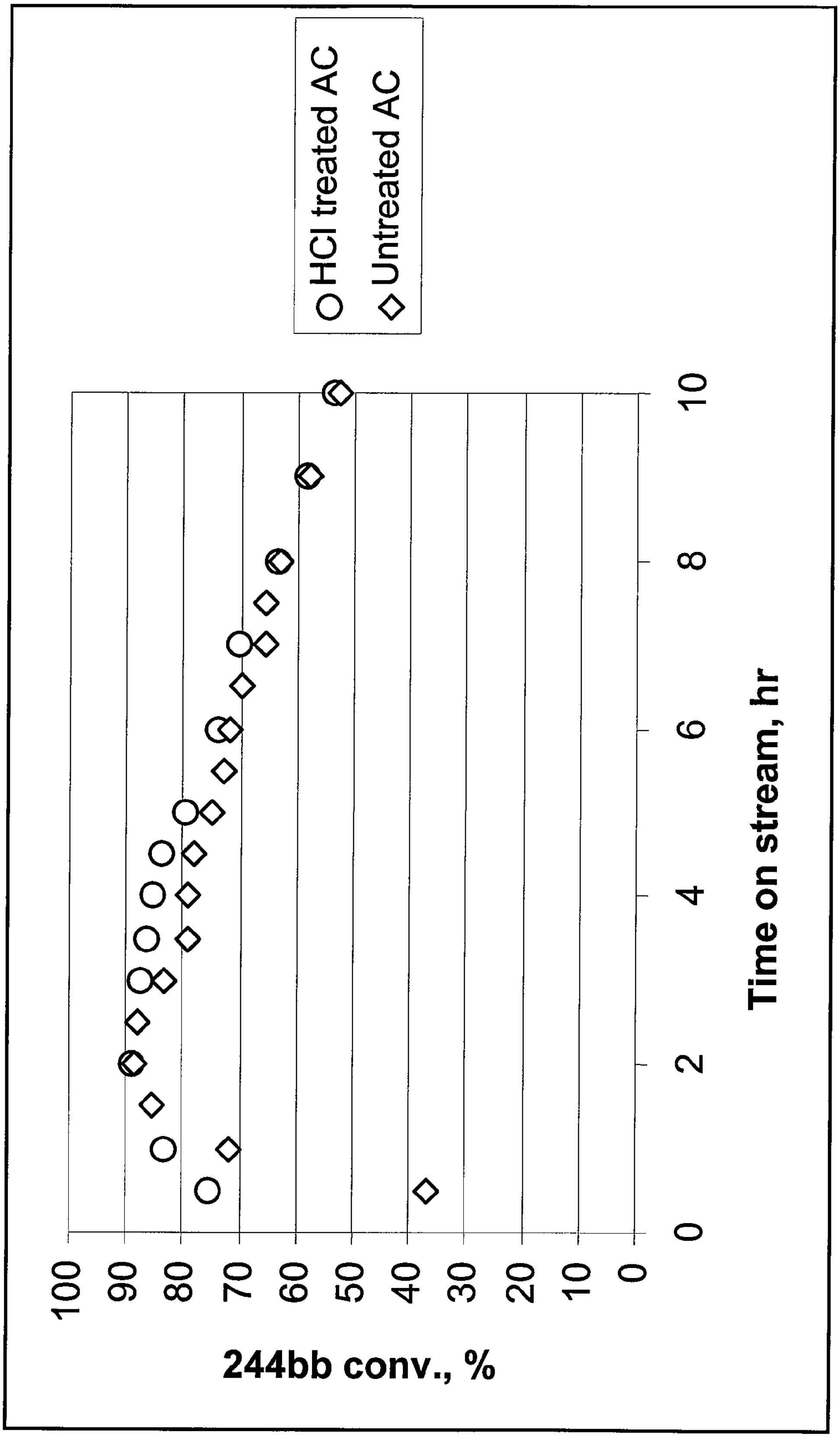
HCl treated AC
Untreated AC
244bb conv., %
100
90
80
70
60
50
40
30
20
10
0
Time on stream, hr
0
2
4
6
8
10

Fig. 1

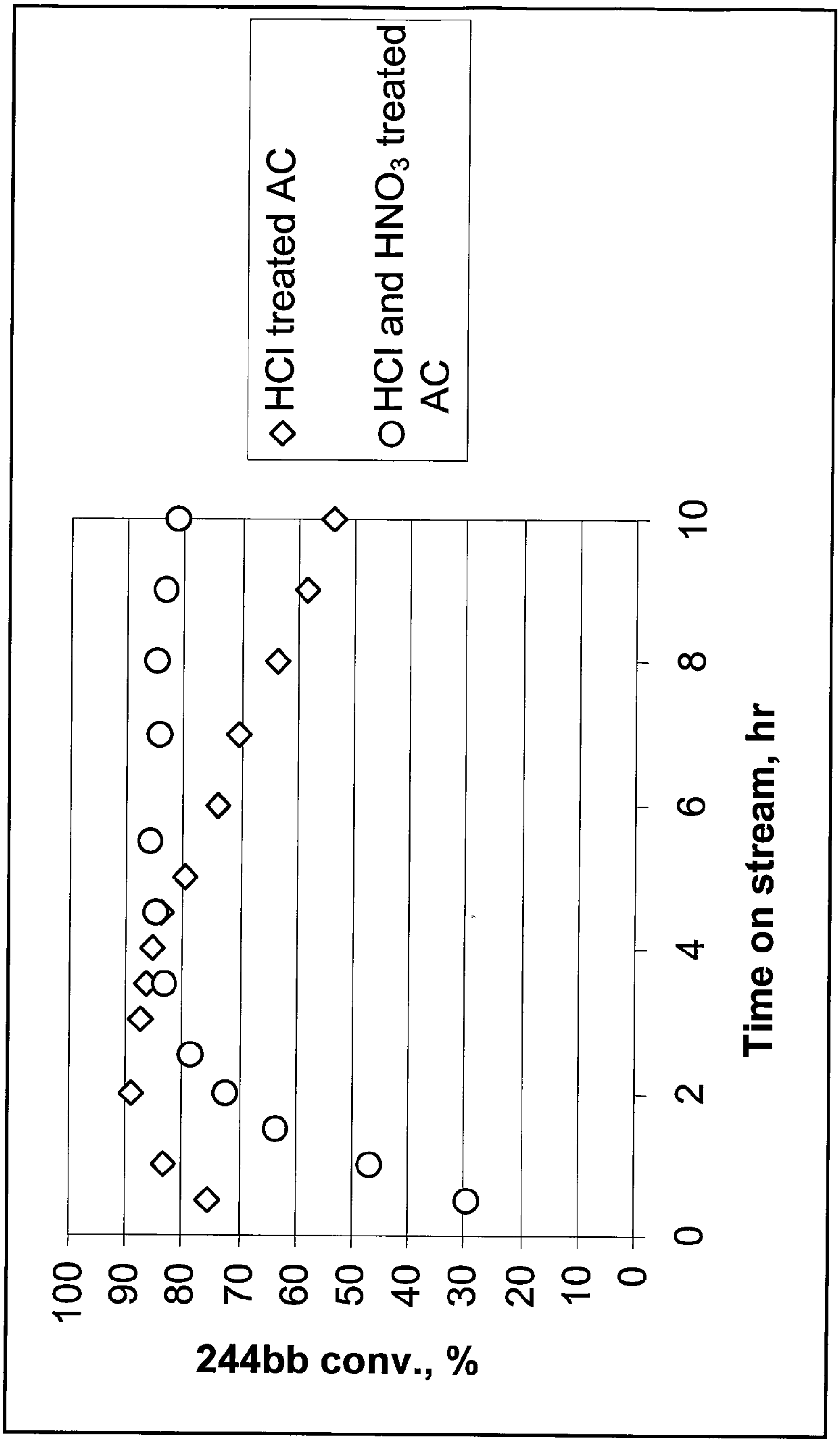
HCl treated AC
HCl and HNO3 treated AC
244bb conv., %
100
90
80
70
60
50
40
30
20
10
0
Time on stream, hr
0
2
4
6
8
10

Fig. 2

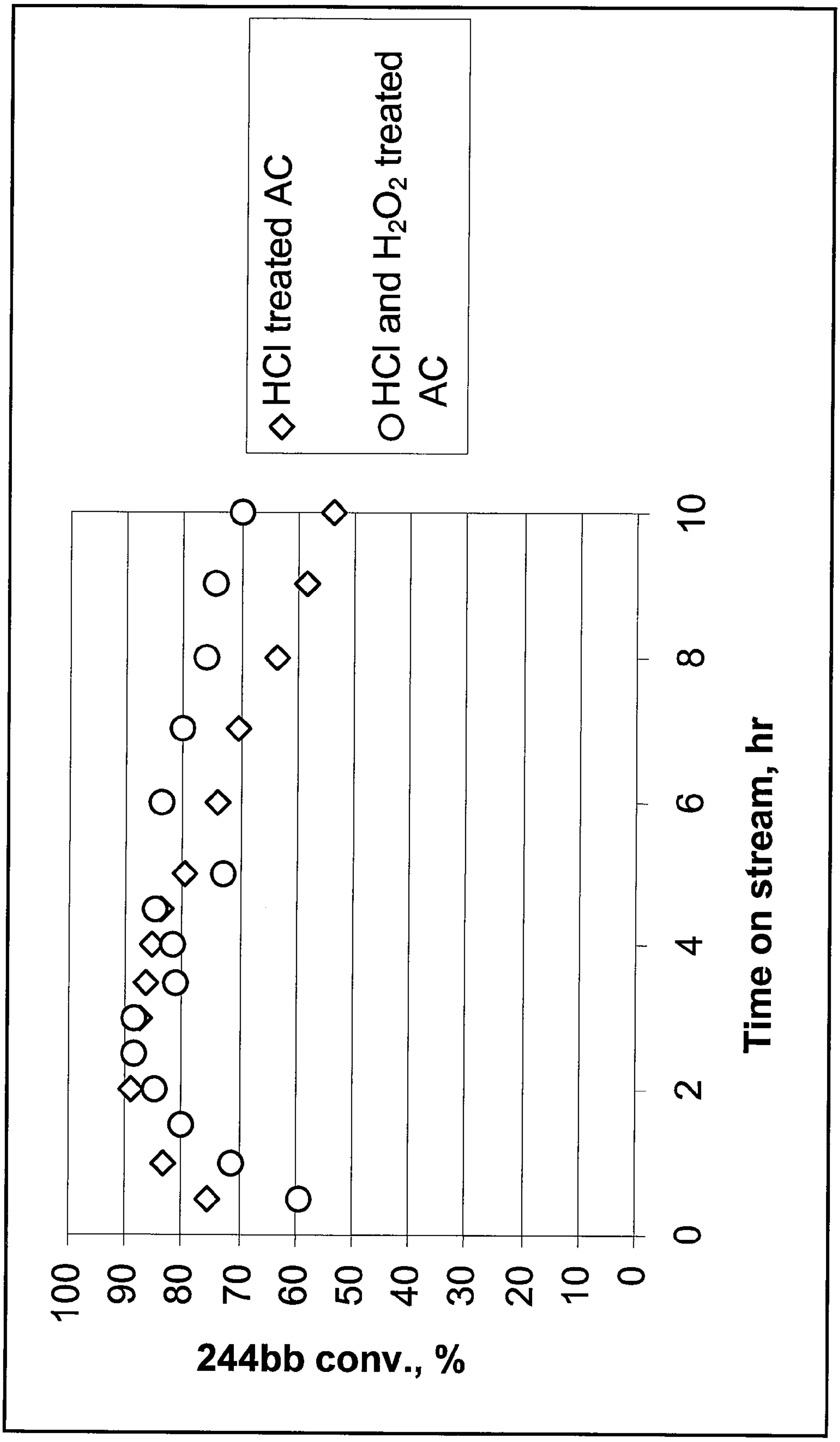
HCl treated AC
HCl and H_2O_2 treated AC
244bb conv., %
100
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
Time on stream, hr

Fig. 3

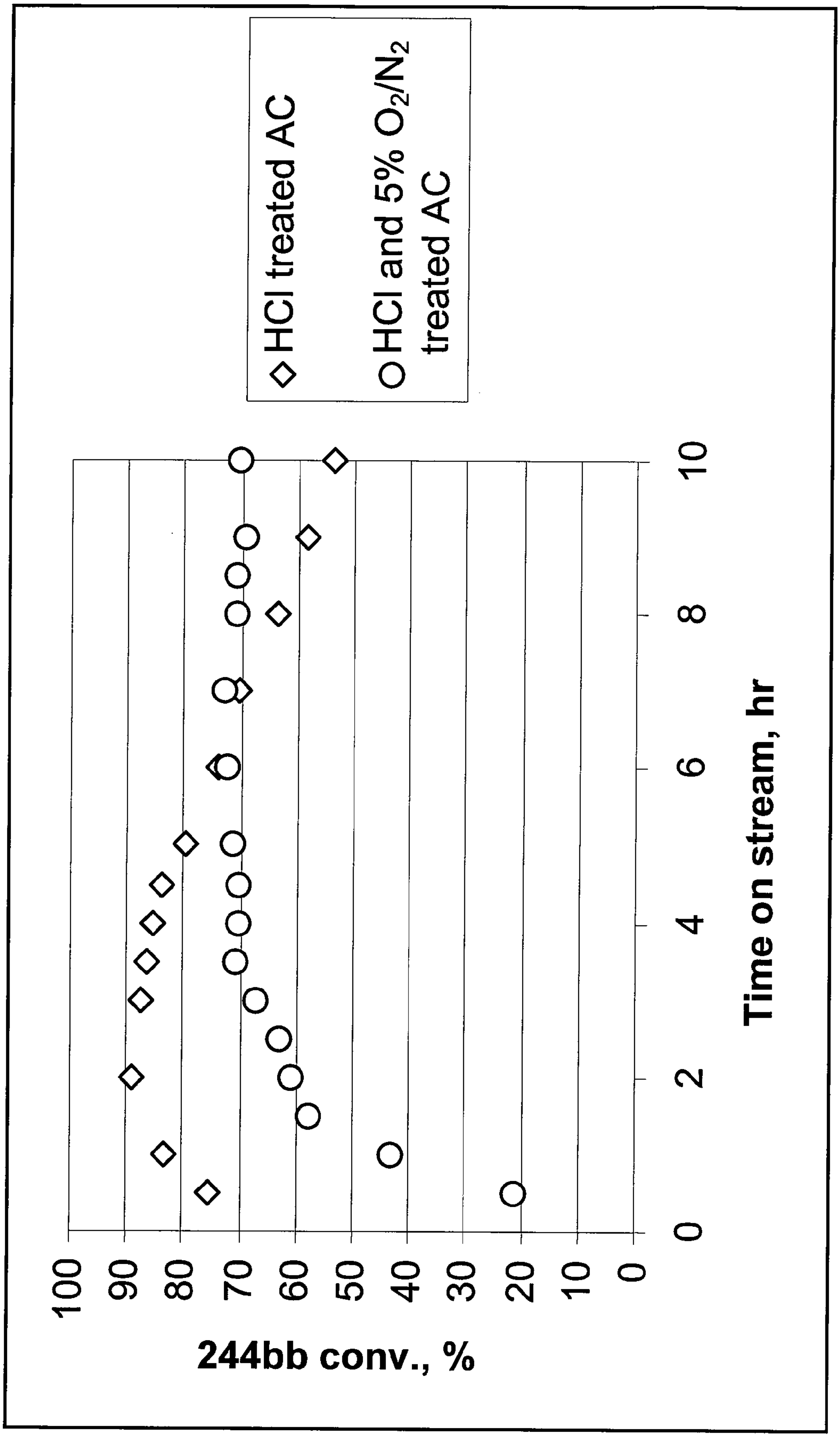
HCl treated AC
HCl and 5% O2/N2 treated AC
244bb conv., %
100
90
80
70
60
50
40
30
20
10
0
Time on stream, hr
0
2
4
6
8
10

Fig. 4

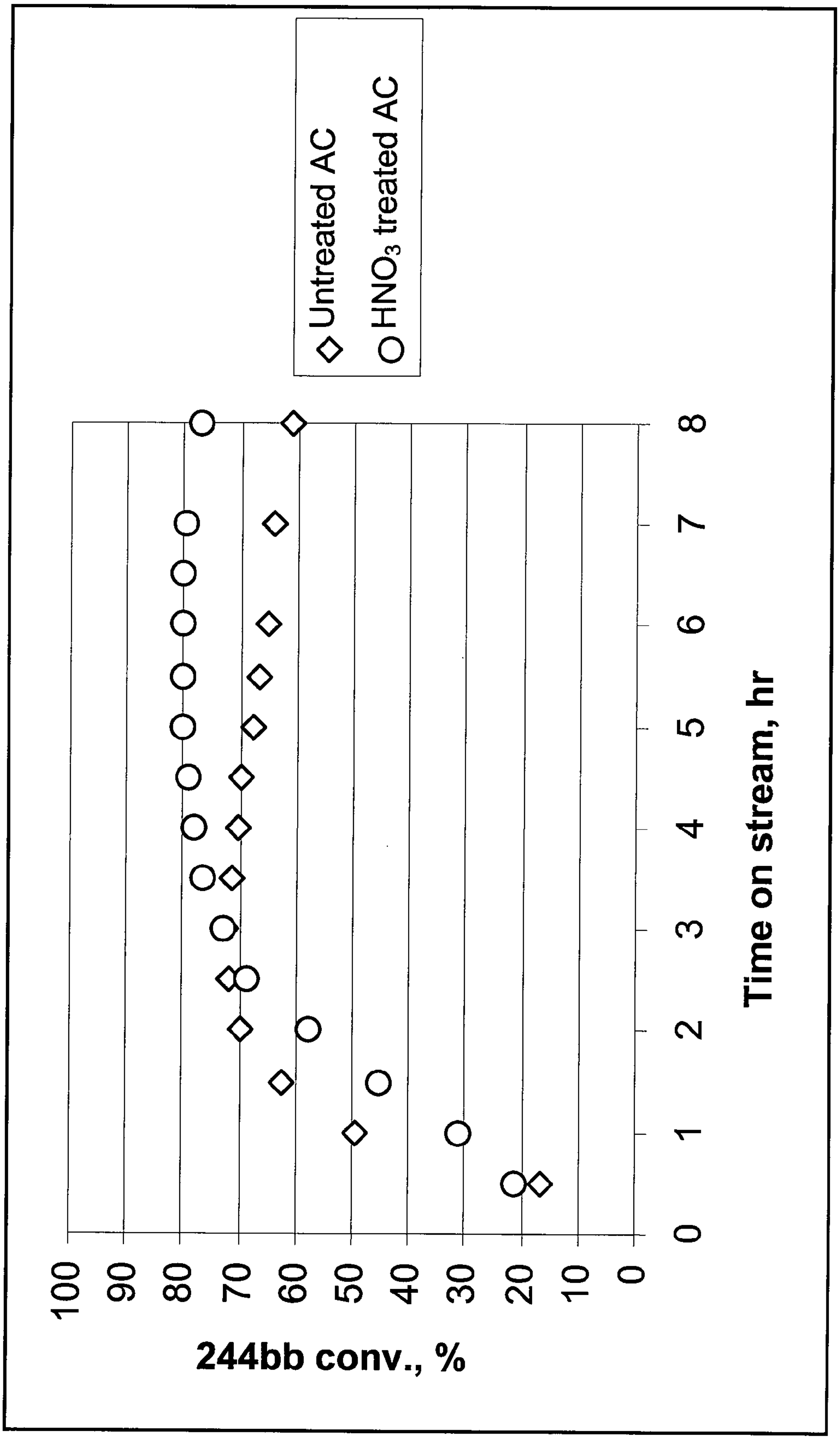
Untreated AC
HNO_3 treated AC
244bb conv., %
100
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
6
7
8
Time on stream, hr

Fig. 5