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United States Patent [19]

Astbury et al.

[11] **Patent Number:** 5,382,741[45] **Date of Patent:** Jan. 17, 1995[54] **PROCESS FOR THE PRODUCTION OF MONO-OLEFINS**[75] **Inventors:** Christopher J. Astbury, London; David C. Griffiths, Surrey; Mark J. Howard, North Humberisde; Ian A. B. Reid, London, all of England[73] **Assignee:** The British Petroleum Company p.l.c., London, England[21] **Appl. No.:** 912,184[22] **Filed:** Jul. 13, 1992[30] **Foreign Application Priority Data**

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[51] **Int. Cl.⁶** C07C 5/333[52] **U.S. Cl.** 585/652; 585/654; 585/658; 585/660[58] **Field of Search** 585/658, 659, 660, 652[56] **References Cited****U.S. PATENT DOCUMENTS**

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OTHER PUBLICATIONSF. M. Ashmaury "Catalytic Oxidative Dehydrogenation . . ." *Journal of Catalysts*, vol. 46, 1977 pp. 424-425.*Primary Examiner*—Asok Pal*Assistant Examiner*—P. Achutamurthy*Attorney, Agent, or Firm*—Nixon & Vanderhye[57] **ABSTRACT**

A process for the production of mono-olefins from a paraffin-containing hydrocarbon feed having at least two carbon atoms which comprises a first step of partially combusting a mixture of the hydrocarbon feed and a molecular oxygen-containing gas in contact with a catalyst capable of supporting combustion beyond the normal fuel rich limit of flammability, the first step being carried out under a total pressure of greater than 5 bar absolute and at a temperature of greater than 650° C.; and a second step of cooling the mono-olefinic products to 600° C. or less within less than 50 milliseconds of formation.

11 Claims, No Drawings

calcined Pt/Pd gamma alumina spheres (2 mm diameter), supported on a silica sintered disk. The preparation of this catalyst is detailed in EP-A-0332289. Propane, hydrogen, oxygen and nitrogen were passed over the catalyst under atmospheric pressure in the molar proportions, and under the conditions, as shown in Table 4. It is evident from these results that high conversion and high selectivity to ethylene is possible under atmospheric pressure provided the residence time is relatively high.

3. A process according to claim 1 in which the catalyst is a supported platinum group metal.

4. A process according to claim 1 in which the platinum group metal is platinum or palladium or a mixture thereof.

5. A process according to claim 4 in which the support is alumina.

6. A process according to claims 1 in which the support is a monolith.

10 7. A process according to claim 1 in which the ratio

TABLE 1

GHSV ($\times 10^6 \text{ hr}^{-1}$)	Total Flow (nl/min)	C ₃ H ₈ /O ₂		Total Pressure (bara)	Residence Time (ms)	Conversion (% mol)	Selectivity (% C mol)					
		C ₃ H ₈ /O ₂	H ₂ /O ₂				C ₂ H ₄	C ₂ H ₂	CH ₄	CO	CO ₂	Coke
3.0	266	1.77	0.94	10.5	20	97.9	36.5	0.4	26.1	19.3	2.1	0
3.1	278	1.96	0.94	10.2	20	95.4	36.6	0.1	24.2	17.4	1.7	0
3.2	280	1.90	1.06	11.0	20	95.6	37.0	0.5	22.0	13.2	2.1	0

TABLE 2

GHSV ($\times 10^6 \text{ hr}^{-1}$)	Total Flow (nl/min)	H ₂ /O ₂	Naphtha/O ₂	Yield (wt % C)												>C ₅ Liquid
				CH ₄	CO	CO ₂	C ₂ H ₄	C ₂ H ₂	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄	C ₅	C ₆ H ₆	C ₆ H ₇	
0.99	2.09	1.12	0.64	12.77	18.43	1.93	26.97	1.06	3.34	9.22	0.53	4.72	3.51	6.31	2.78	8.45
0.99	2.09	1.12	0.64	13.12	19.71	1.50	25.70	1.08	3.18	7.27	0.43	2.90	3.87	5.33	3.49	12.49
0.99	2.09	1.12	0.64	13.21	19.30	1.47	25.71	1.08	3.03	7.57	0.43	3.39	5.07	7.93	0.85	10.95
0.99	2.09	1.12	0.64	12.08	18.52	1.28	25.37	0.80	3.34	8.84	0.49	4.16	2.26	6.78	4.30	11.78

TABLE 3

GHSV ($\times 10^6 \text{ hr}^{-1}$)	Total Flow (nl/min)	C ₃ H ₈ /O ₂		Total Pressure (bara)	Residence Time (ms)	Conversion (% mol)	Selectivity (% C mol)					
		C ₃ H ₈ /O ₂	H ₂ /O ₂				C ₂ H ₄	C ₂ H ₂	CH ₄	CO	CO ₂	Coke
3.0	268	1.72	0.91	10.5	220	99.6	11.1	0.1	38.9	19.0	7.2	16.0
3.1	278	1.96	0.94	11.8	220	99.2	8.8	0.1	36.9	24.8	3.7	17.0

TABLE 4

GHSV ($\times 10^6 \text{ hr}^{-1}$)	Total Flow (nl/min)	C ₃ H ₈ /O ₂		Total Pressure (bara)	Residence Time (ms)	Conversion (% mol)	Selectivity (% C mol)			
		C ₃ H ₈ /O ₂	H ₂ /O ₂				C ₂ H ₄	C ₂ H ₂	CH ₄	CO ₂
0.3	26	1.99	1.22	1	30	75.8	39.9	0.7	16.1	9.7
0.3	26	1.98	1.22	1	60	86.9	43.2	1.0	18.4	9.9
0.3	26	2.01	1.20	1	90	91.0	43.8	1.4	19.1	10.2
0.3	26	1.94	1.20	1	120	92.4	44.9	1.3	19.7	10.6

We claim:

1. A process for the production of mono-olefins from a paraffin-containing hydrocarbon feed having at least two carbon atoms, the process comprising:

(a) a first step of partially combusting a mixture of the hydrocarbon feed and a molecular oxygen-containing gas in contact with a combustion catalyst, said first step carried out under a total pressure of greater than 5 bar absolute, and at a temperature of greater than 650° C., and

(b) a second step of cooling the mono-olefinic products to 600° C. or less within less than 50 milliseconds of formation.

2. A process according to claim 1 in which the hydrocarbon feed is ethane, propane, butane, naphtha, gas oil, vacuum gas oil or mixtures thereof.

of the hydrocarbon feed to the molecular oxygen is from 5 to 13.5 times the stoichiometric ratio of hydrocarbon to oxygen for complete combustion to carbon dioxide and water.

8. A process according to claim 1 in which the gaseous feed is introduced at a gas hourly space velocity of at least 80,000 hr⁻¹.

9. A process according to claim 1 in which the olefinic product is cooled using rapid heat exchangers or a direct quenching fluid.

10. A process according to claim 9 in which the direct quenching fluid is selected from water or a hydrocarbon compound.

11. A process according to claim 10 in which the hydrocarbon compound is a naphtha compound.

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