A theory is presented which postulates that the double-α is the sum of two growth processes, one a stepwise single-carbon growth process (the α_1 mechanism) and the other the sum of the 1-alkene incorporation processes (the α_2 mechanism). Many of the effects of process variables on the hydrocarbon selectivity of Fischer-Tropsch catalysts are consistent with this model.

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Nomenclature

$f_{1,2}$ - parametric constants for ethene propagation model.

M_{added} - mole fraction of products at carbon number of added alkene.

M_o - constant, the mole fraction of products at carbon number "zero".

M_n - mole fraction of products at carbon number n.

n - carbon number.

Normalized(M_n) - normalized mole fraction, with M_{added} removed.

Observed(M_n) - mole fraction data, observed experimentally.

p_1 - the probability of C_1 addition.

p_2 - the probability of C_2 initiation or termination.

p_3 - the probability of C_3 initiation or termination.

x_1 - mole fraction of products produced by α_1 mechanism.

Greek

α - single chain growth probability.

α_1 - chain growth probability for stepwise addition of C_1.

α_2 - chain growth probability for incorporation of alkenes.

Γ - ratio of reactivity of C_2/C_1.

Θ_1 - mole fraction of C_1.

Θ_2 - mole fraction of C_2.

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TABLE 1

INTERPRETATION OF OBSERVED PROCESS VARIABLE EFFECTS ON COBALT

Process variable	Effect on yield to desired products	Postulated explanation based on incorporation of 1-alkenes
Decreasing space velocity (increasing conversion)	Decreases yield of desired heavy products	At low space velocities, 1-alkenes are converted to n-alkanes and 2-alkenes more readily.
Increasing H_2/CO ratio	Decreases yield of desired heavy products	At high H_2/CO ratio, 1-alkenes are more readily hydrogenated and therefore less are incorporated.
Pressure	No effect	1-alkene reactions are affected predominantly by the ratio of reactant pressures, not total pressure.
Temperature	No effect	The rate of incorporation and of competing reactions such as hydrogenation and isomerization are affected by temperature similarly.

Figure Captions

Figure 1a Ethene incorporates into growing chains on cobalt. Ethene added to comprise 0.64 mol.% of feed (220°C, 1.48 MPa. Entering H_2/CO = 2.15, (H_2/CO) in reactor ~ 2.2. Feed rate = 0.030 Nl/min/gcat (unreduced basis)).

Figure 1b Propene incorporates into growing chains on cobalt. Propene added to comprise 0.70 mol.% of feed (220°C, 1.48 MPa. Entering (H_2/CO)=1.61, (H_2/CO) in reactor ~ 1.59. Feed rate = 0.029 Nl/min/gcat (unreduced basis)).

Figure 1c 1-butene incorporates into growing chains on cobalt. 1-butene added to comprise 0.64 mol.% of feed (220°C, 1.48 MPa. Entering (H_2/CO) = 2.15, (H_2/CO) in reactor ~ 2.17. Feed rate = 0.030 Nl/min/gcat (unreduced basis)).

Figure 2a Hydrogenation decreases incorporation of ethene. Comparing the vertical axis values for this plot with Figures 2b and 2c indicates that ethene incorporates more than propene or 1-butene.

Figure 2b Propene incorporates into growing chains. Propene incorporates less than ethene, but more than 1-butene (see Figure 2a and 2c).

Figure 2c 1-butene incorporates into growing chains. 1-butene incorporates less than either ethene or propene (see Figure 2a and 2b).

Figure 3 Methanation rate is unaffected by alkene additions. (220°C, 0.5 to 1.5 MPa.)

Figure 4 Hydrocarbon selectivity was stable throughout alkene addition experiments (220°C, 0.79 MPa. Entering (H_2/CO)=1.62, (H_2/CO) in reactor ~ 1.65. Feed rate = 0.017 Nl/min/gcat (unreduced basis)).

Figure 5 Model accounting for initiation and termination by C_2 and C_3 alkenes appears similar to single-α model, except at low carbon numbers (p_1=0.7, p_2=0.3, and p_3= 0.1).

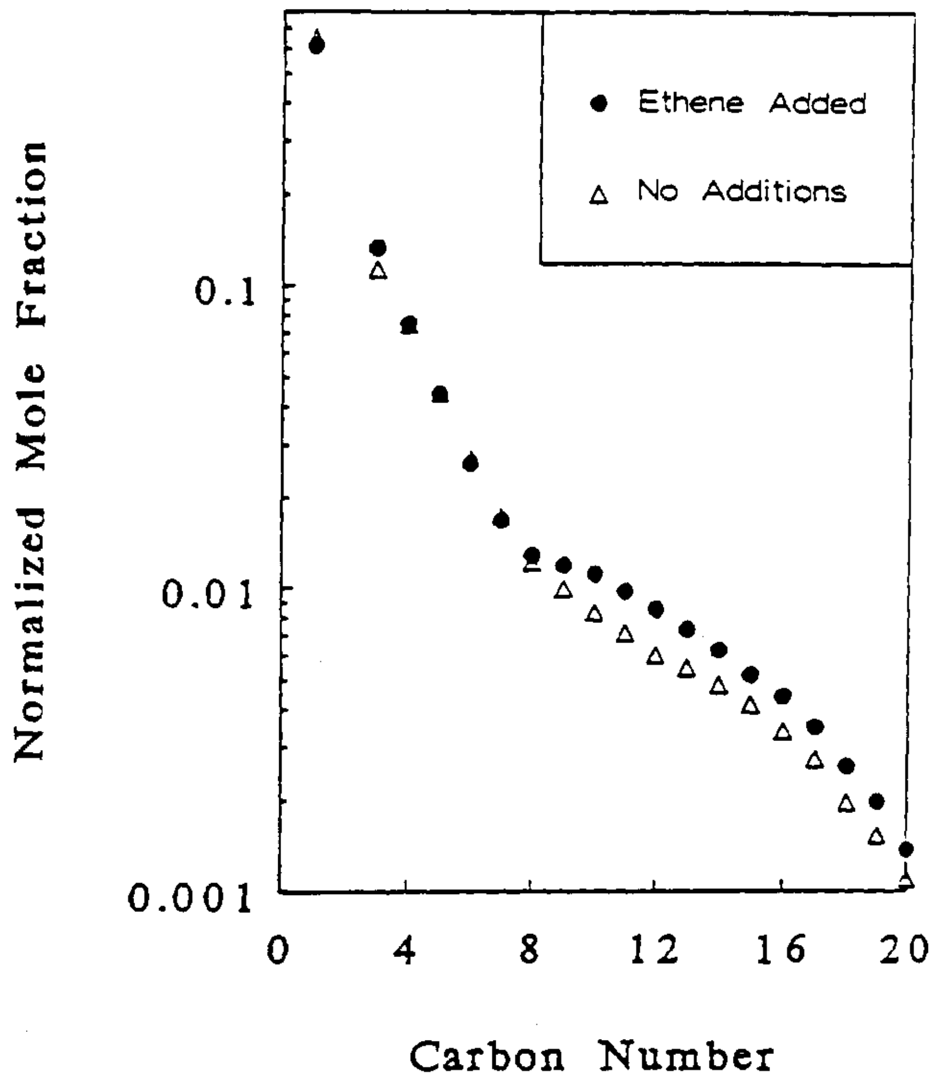
Figure 6 Model accounting for initiation, termination, and propagation by ethene appears similar to single-α model, except at low carbon numbers (Θ_1=0.5, Θ_2=0.1, α=0.62, and Γ=0.2).

Figure 7 Fitting of ethene addition results to a model which accounts for separate contributions by a stepwise growth process and a 1-alkene incoproration process. (Same data as Figure 1a).

Figure 8 Alkene addition data can be interpreted by a model which accounts for separate contributions by a stepwise growth process and a 1-alkene incorporation process. (Same data as Figure 1a).

Figure 9 Space velocity affects the yield of C_1 (undesired) and C_{10}+ (desired). Data labels show the *in situ* ethene to ethane ratio.

Figure 10 (H_2/CO) ratio affects the yield of desired C_{10}+. Data labels show the *in situ* ethene to ethane ratio. Effect is consistent with hypothesis that α_2 is caused by incorporation processes.



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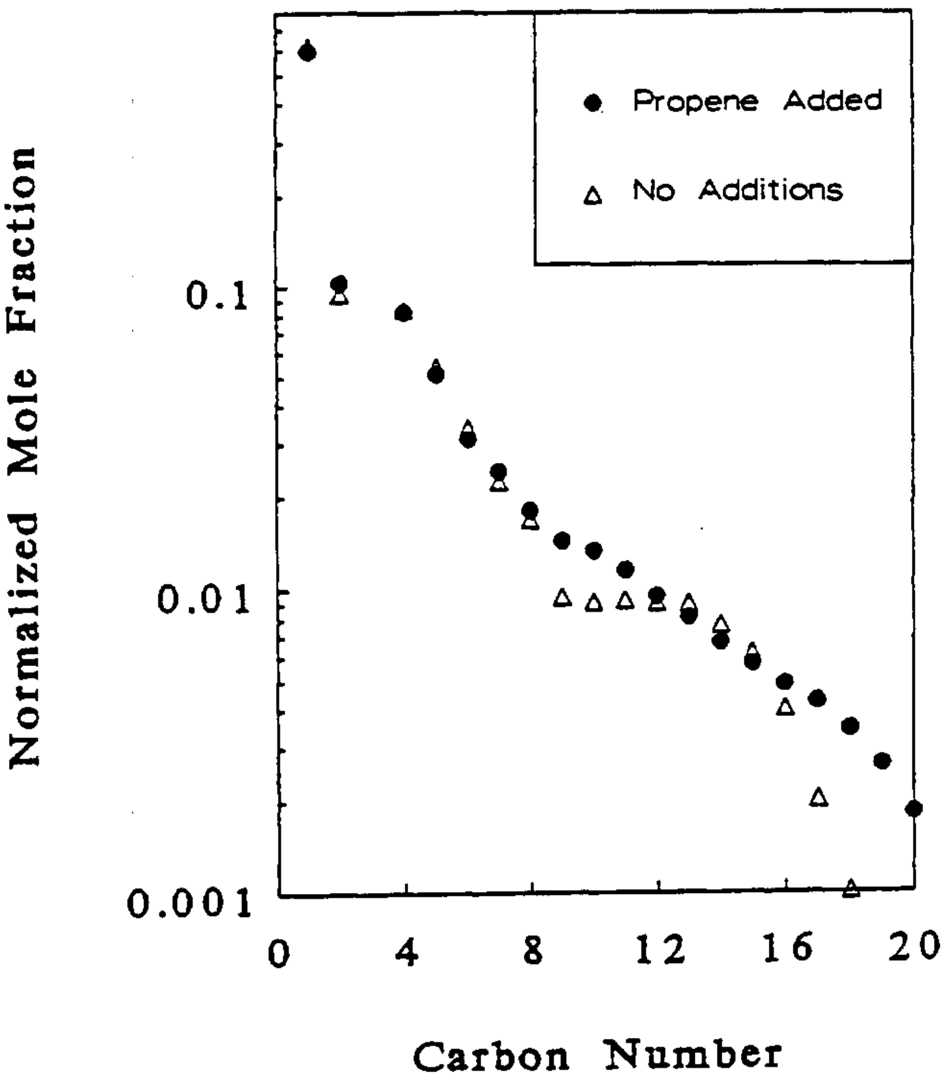

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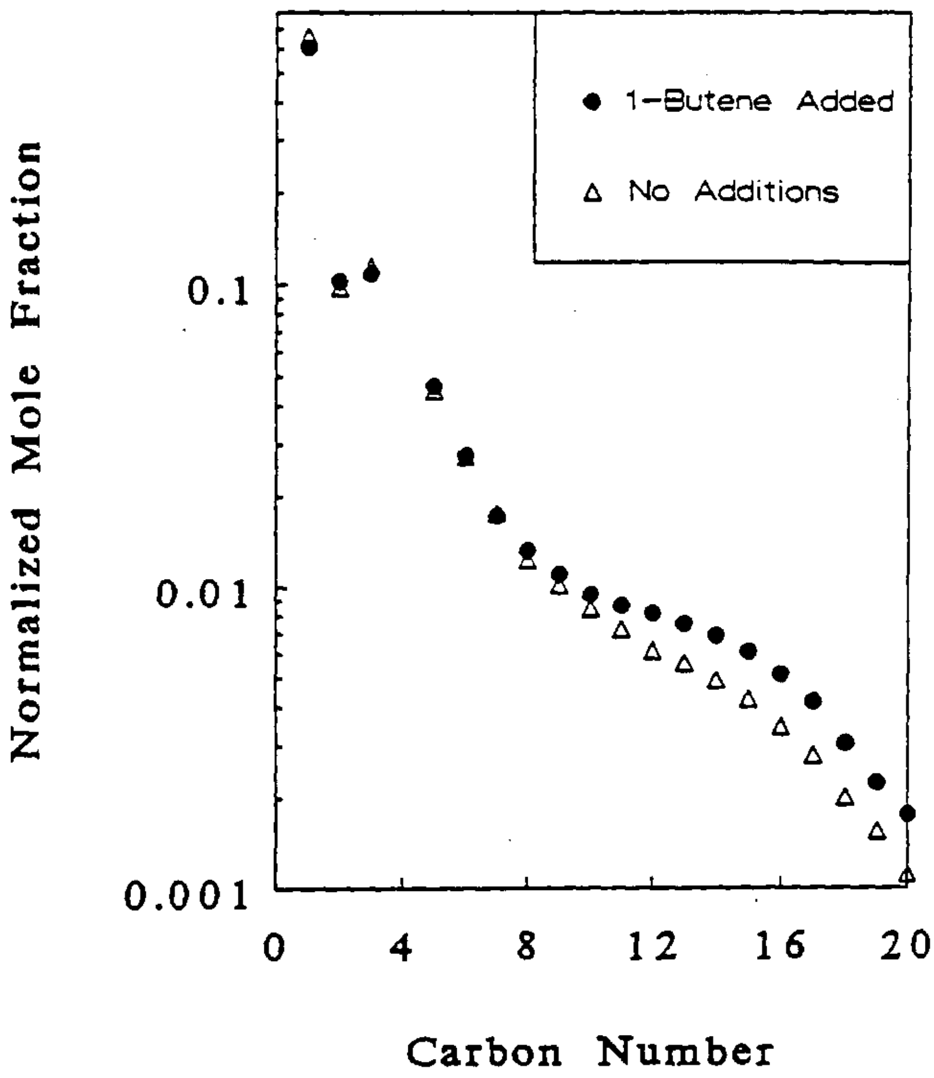

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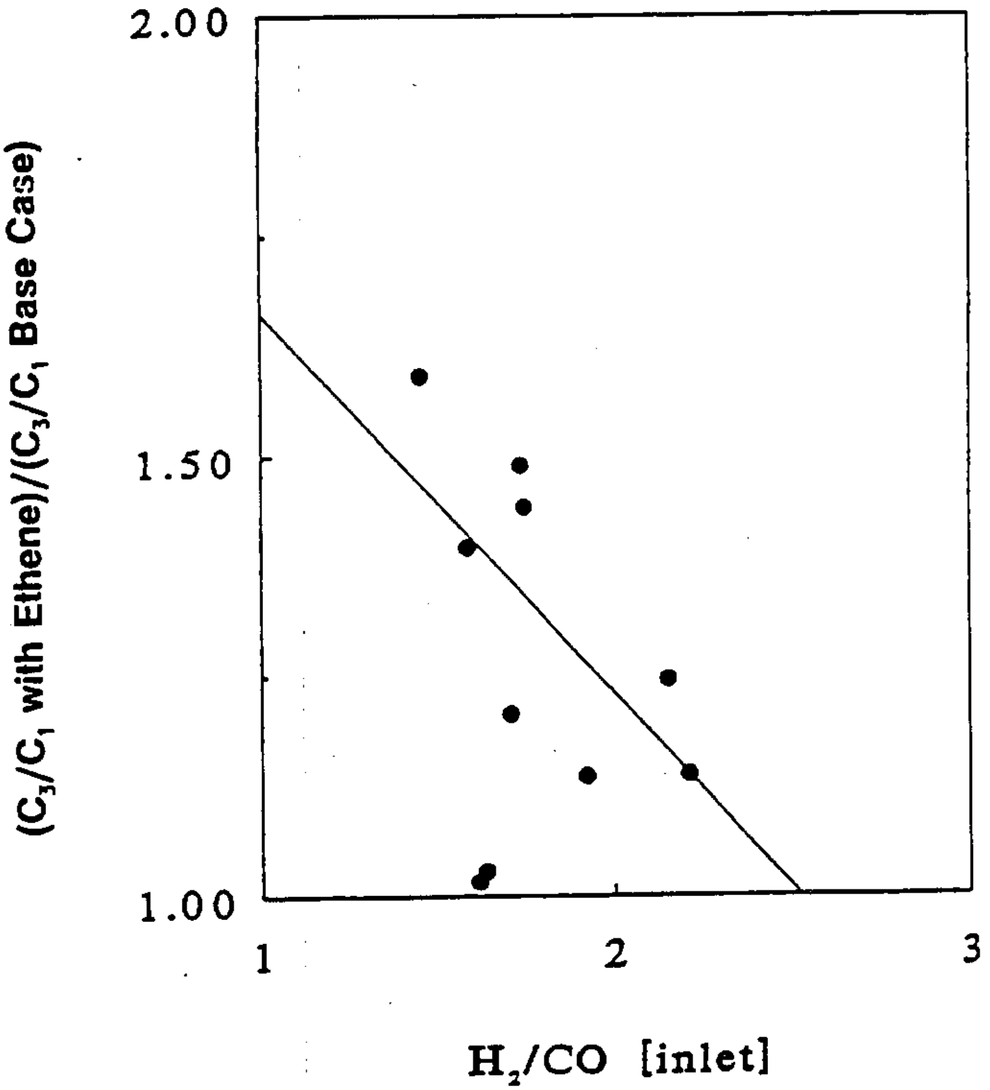

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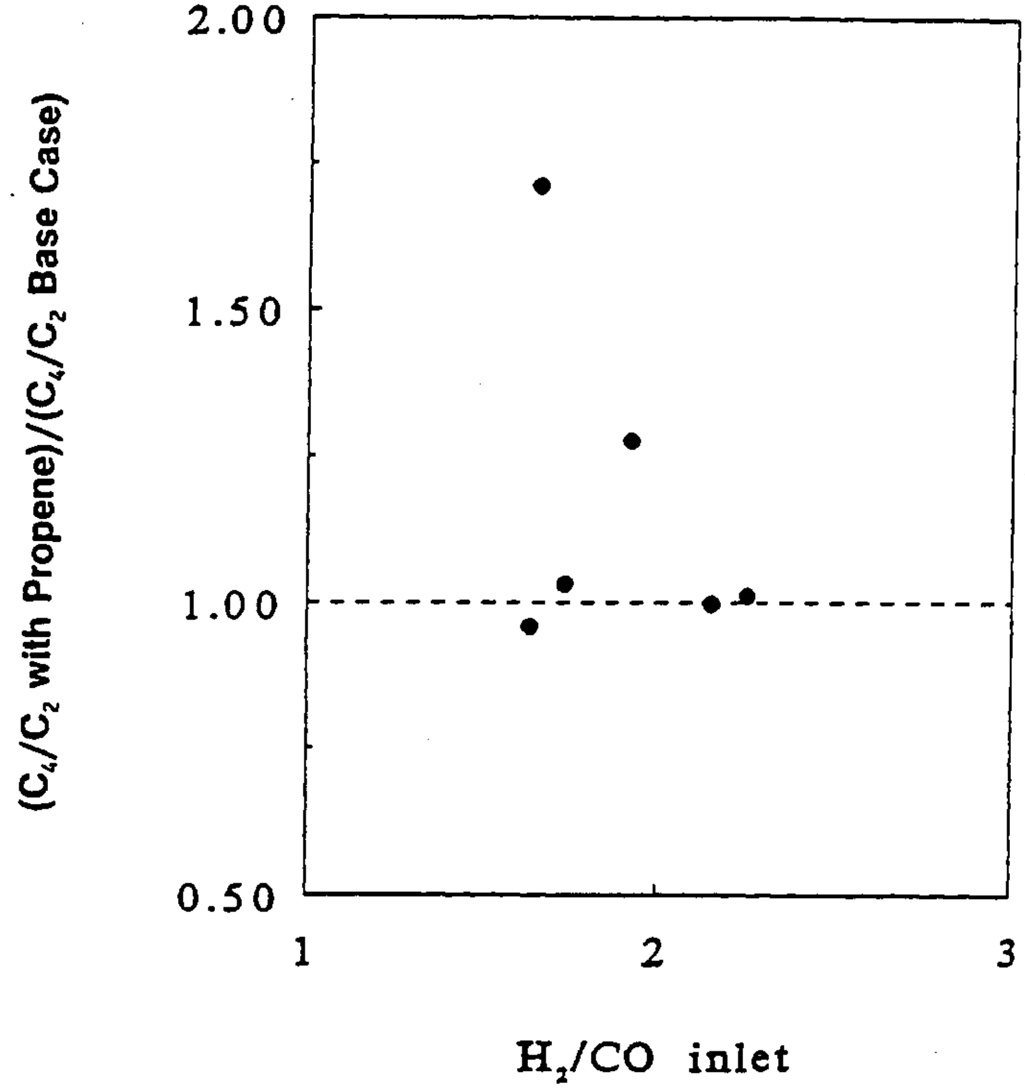

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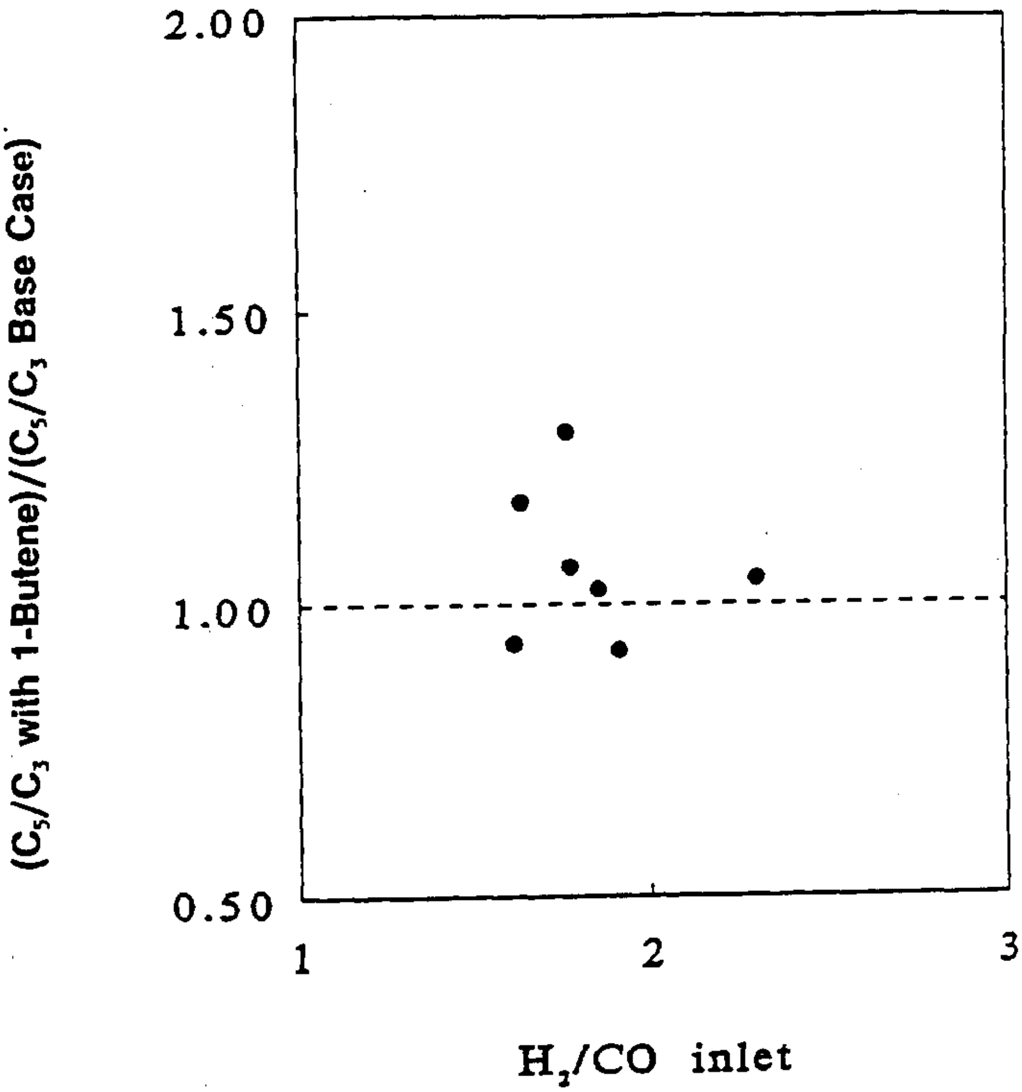

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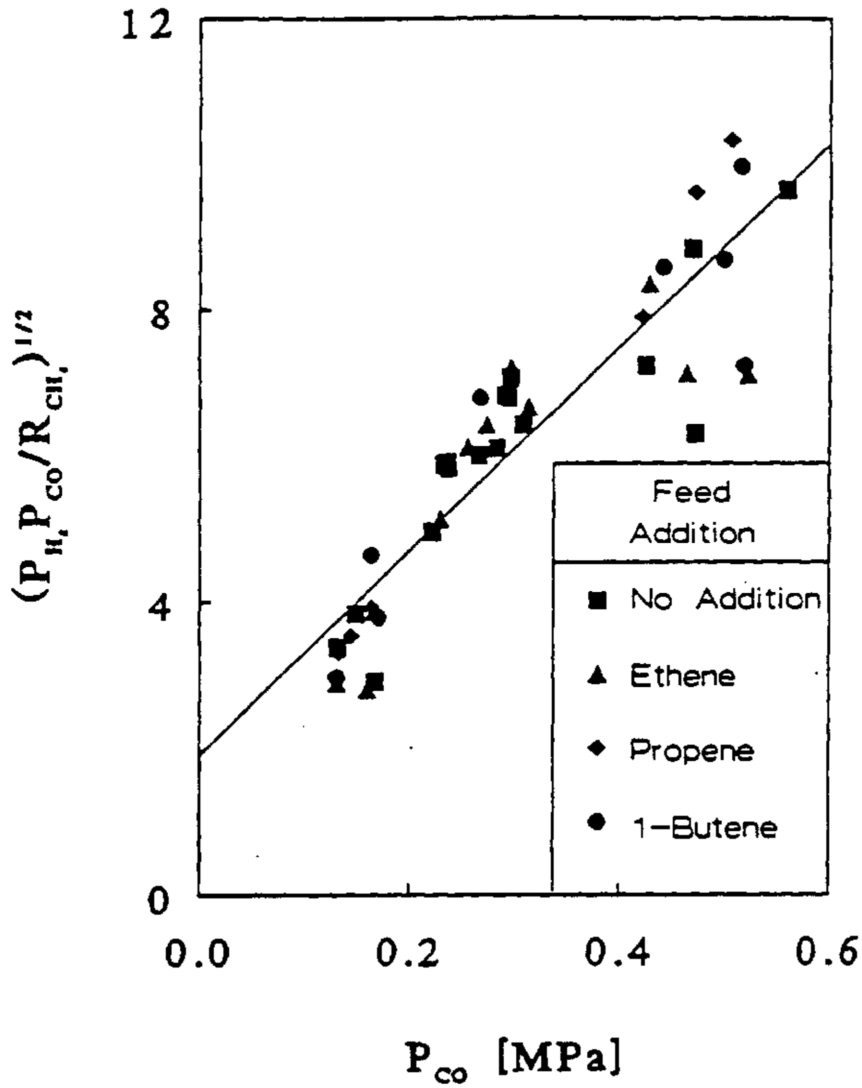

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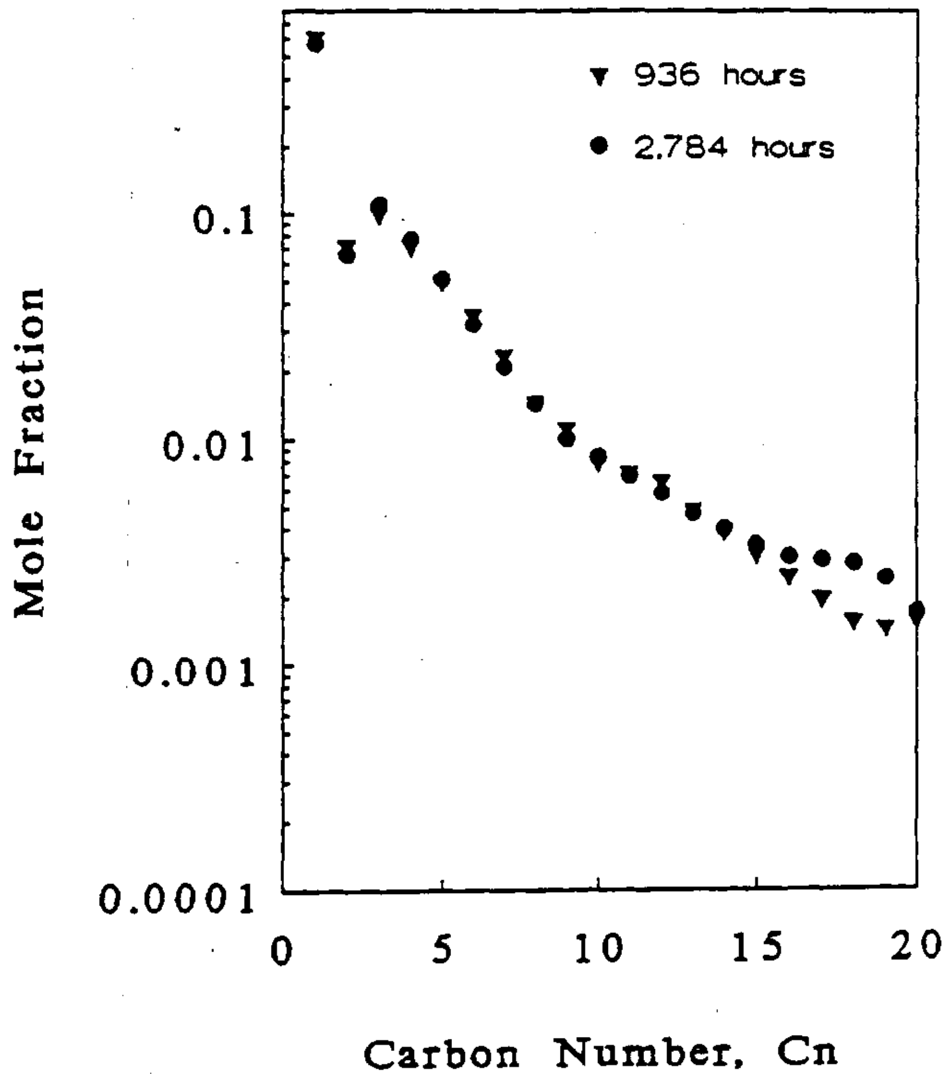

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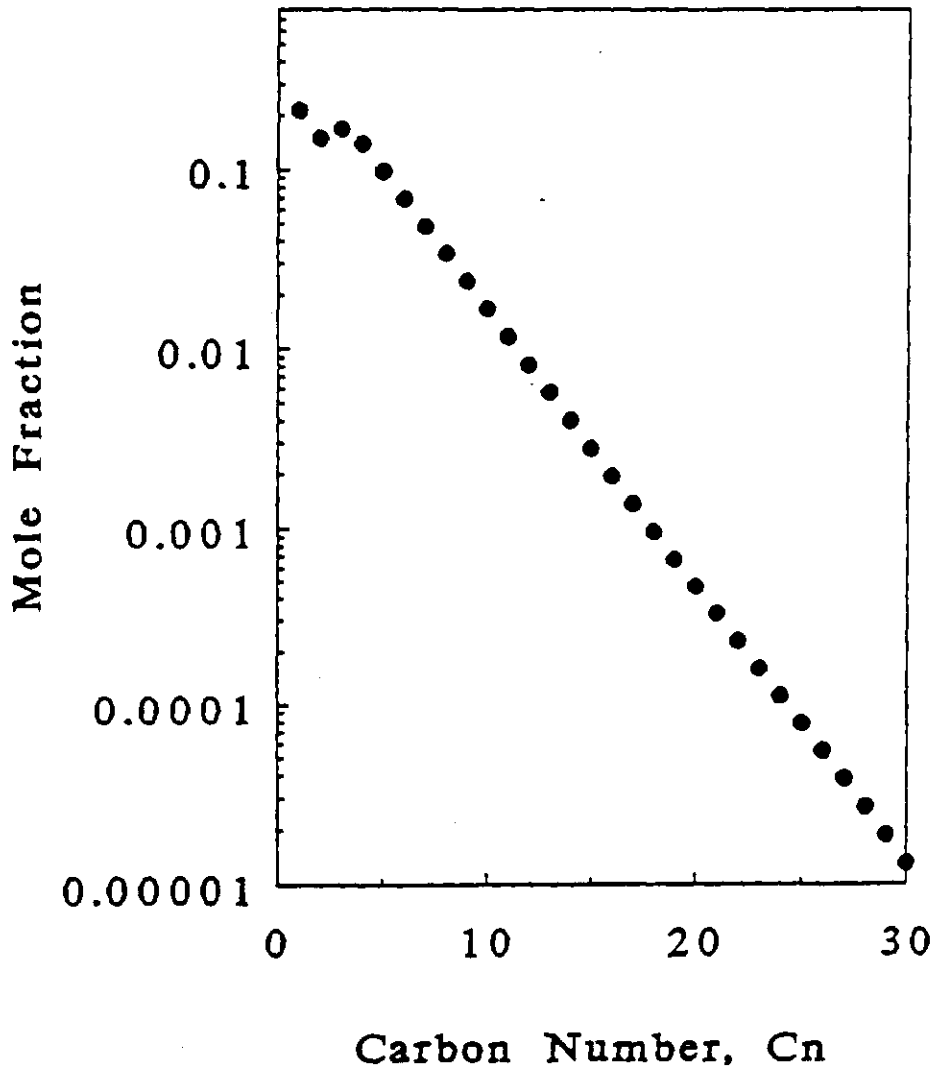

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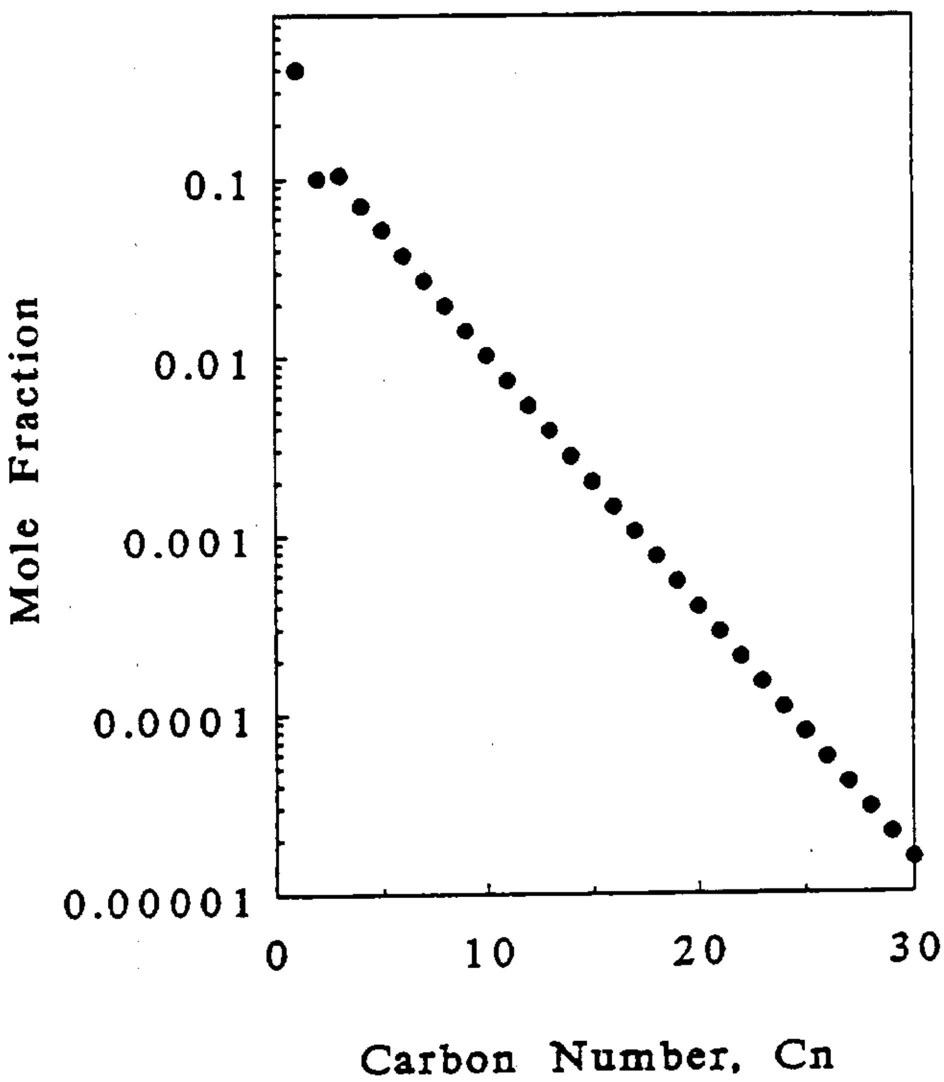

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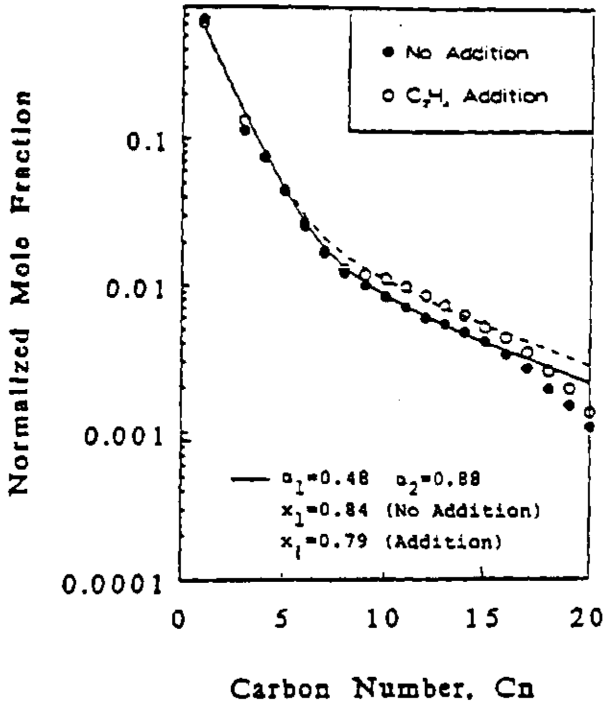

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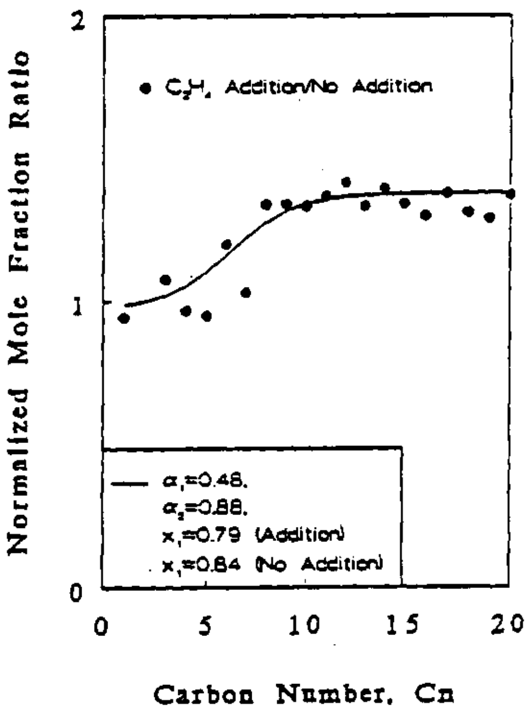

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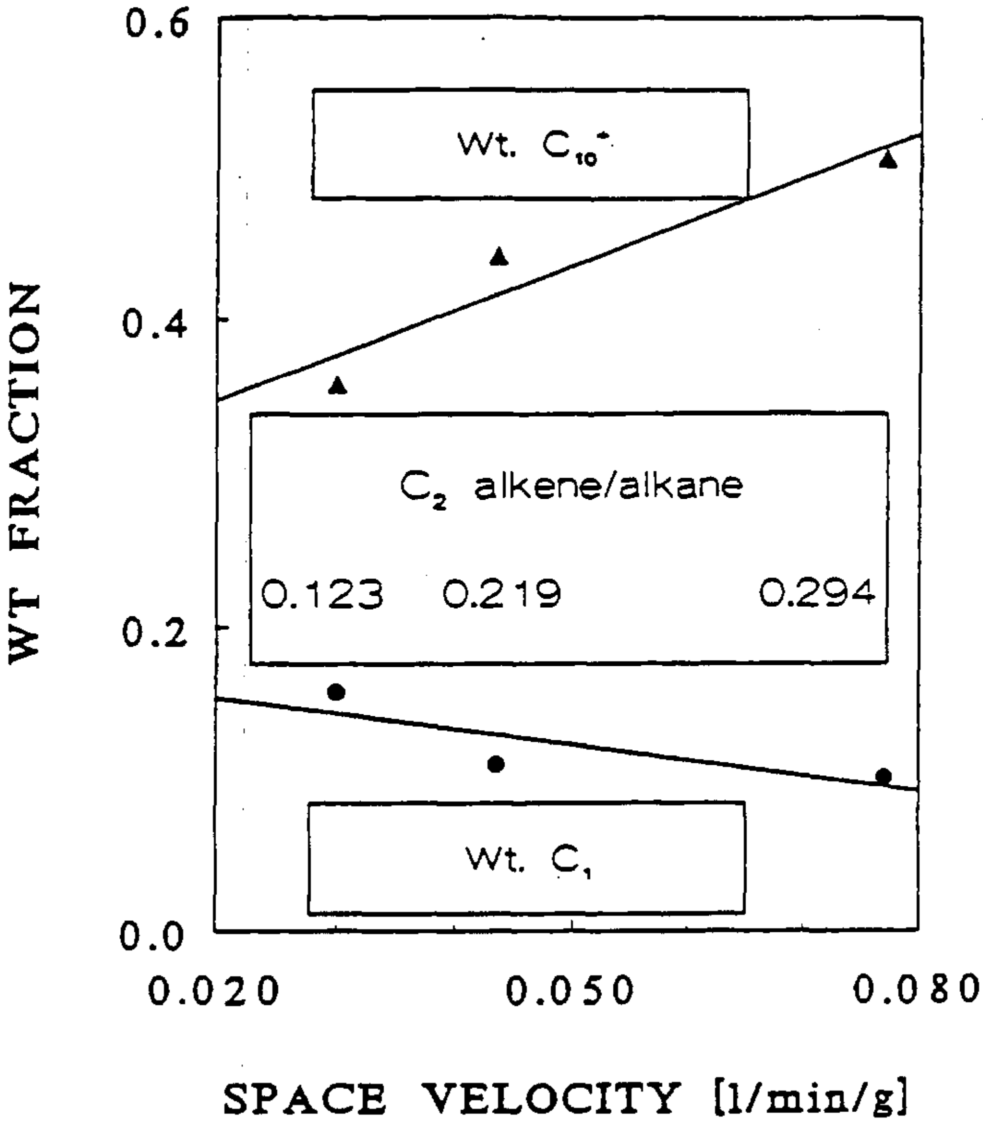

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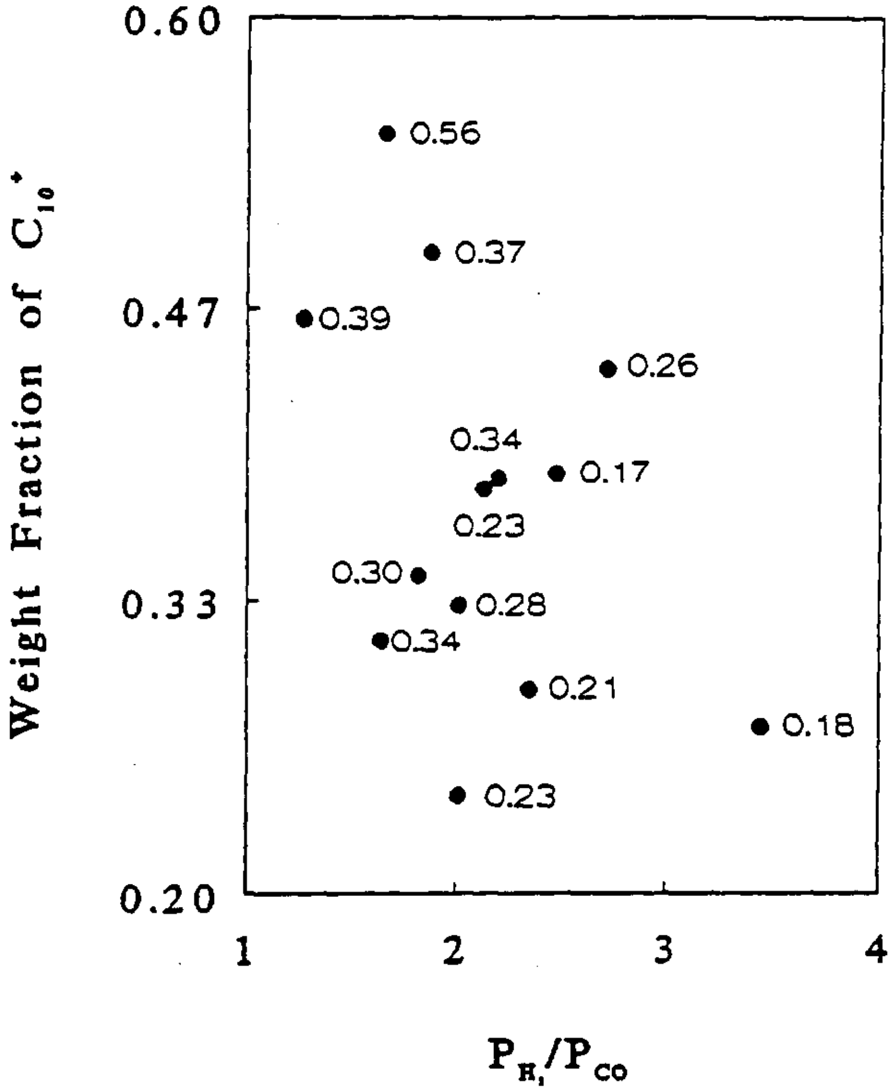

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