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MODELING OF THE SILANE FBR SYSTEM

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Objectives

- Development of a mathematical model for fluidized bed pyrolysis of silane that relates production rate and product properties (size, size distribution, presence or absence of fines) with bed size and operating conditions (temperature, feed concentration flow rate, seed size, etc.).
- Development of user oriented algorithm for the model.
- Parameter sensitivity study of the model.

Needed

- Assumptions on mixing pattern of gas and solids.
- Mass and energy balances for gas and solid phase.
- Constitutive relationships
  - Homogeneous nucleation rate
  - CVD growth
  - Fines interactions
  - Scavenging of fines by large particles
  - Transport properties in fluidized beds

Summary of Work Done

1. The kinetic studies on silane pyrolysis were reviewed and all pathways and rate models for Si formation via silane pyrolysis were summarized. A CVD growth and homogeneous rate form were selected.

2. A simplified model was developed assuming the reactor to be completely mixed. This model was solved for both batch as well as continuous feed of solids with/without homogeneous nucleation.

3. A computer program was developed for a more general fluidized bed model based on the modified two phase theory accounting for CVD growth only.

4. A detailed model based on population balance approach was developed for predicting particle size distribution of fines when CVD growth, coagulation, scavenging by seed particles and homogeneous nucleation take place.

Back-Mixed Reactor Model

(1) Balance on SiH_4 (g)

$$q_f C_{s,f} - q_e C_{s,e} = V\bar{r}_{HT,1} + V\bar{r}_{HT,2} + Vr_{HO}$$

where

$V\bar{r}_{HT,1} \equiv$ total rate of CVD on seed particles

$$= N_s \cdot 4\pi R^2/\phi_s \cdot r_{HT}$$

$$r_{HT} = A \exp(-\Delta E/R_g T_p)\, C_{s,e}$$

$V\bar{r}_{HT,2} \equiv$ total rate of CVD on fines

$Vr_{HO} \equiv$ total rate of homogeneous nucleation

(2) Balance on seed solids (uniform particle size)

$$\frac{dR}{dt} = \frac{r_{HT}}{\phi_s}\frac{M_{si}}{\rho_{si}} + \frac{m_{sca}}{4\pi R^2\, N_S \rho_{si}}$$

where $m_{sca} \equiv$ total rate of scavenging

$$= \rho_{si} \int_{v^*}^{v_{max}} v\, \alpha(v)\, n(v,t)\, dv$$

(3) Energy balance

4) **Balance equation for fines**

$$\frac{\partial\, n(v,t)}{\partial t} + R_{elu}(v,t) + \frac{\partial}{\partial v}\,[I(v,t)\; n(v,t)]$$

$$= \int_{v^*}^{v/2} \beta(v-\tilde{v},\tilde{v})\; n(v-\tilde{v},t)\; n(\tilde{v},t)\; d\tilde{v}$$

$$- \int_{v^*}^{v_{max}} \beta(v,\tilde{v})\; n(v,t)\; n(\tilde{v},t)\; d\tilde{v}$$

$$- R_{sca}(v,t) + S(v,t)$$

where

$I(v,t)$	$\equiv$	rate of particle growth = dv/dt
$\beta(v,\tilde{v})$	$\equiv$	the coagulation coefficient
$R_{elu}(v,t)$	$\equiv$	rate of elutriation = $K(v)\cdot n(v,t)$
$R_{sca}(v,t)$	$\equiv$	rate of scavenging = $\alpha(v)\cdot n(v,t)$
$S(v,t)$	$\equiv$	rate of generation of fines by homogeneous nucleation = $S_o\cdot\delta(v-v^*)$

Define the total volume by the first moment:

$$M_1(t) = \int_{v^*}^{v_{max}} v\; n(v,t)\; dv$$

For t e special case:

$$K(v) = \text{const. } K$$

$$I(v,t) = \sigma_1 v$$

$$\beta(v,\tilde{v}) = \beta_1 (v + \tilde{v})$$

$$\alpha(v) = \text{const. } \alpha$$

$$M_1(t) = \left[\frac{S_o\; v^*}{\sigma_1 - (\alpha + K)}\right]\left(e^{[\sigma_1 - (\alpha + K)]t} - 1\right)$$

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Input Data (From JPL 6-in. FBR Experiments)

1. Reactor Specifications

bed diameter	= 15.4 cm (6.065" I.D.)
no. of orifice holes	= 4500
orifice area	= 0.02 cm^2

2. Operating Conditions

total pressure of gas	= 1.34 atm
total volumetric flow rate	= 600 cm^3/s - 1200 cm^3/s (1.97 moles/min - 3.94 moles/min)
feed ratio of SiH_4	= 20% - 80%
Initial total wt. of seed solids	= 10 to 12 kg
Initial diameter of seed solids	= 200 - 240 μm
entering gas temp.	= 25°C
wall temp.	= 600 - 800°C
distributor plate temp.	= 200°C

Back-Mixed Reactor Model

Bed parameters needed

h_w	-	heat transfer coefficient between bed and wall	Wender and Cooper (1958)
h_d	-	heat transfer coefficient between bed and distributor plate	
H_{mf}	-	bed height at minimum fluidizing conditions	Kunii and Levenspiel (1969)
K(R)	-	elutriation constant	Wen and Hashinger (1960)

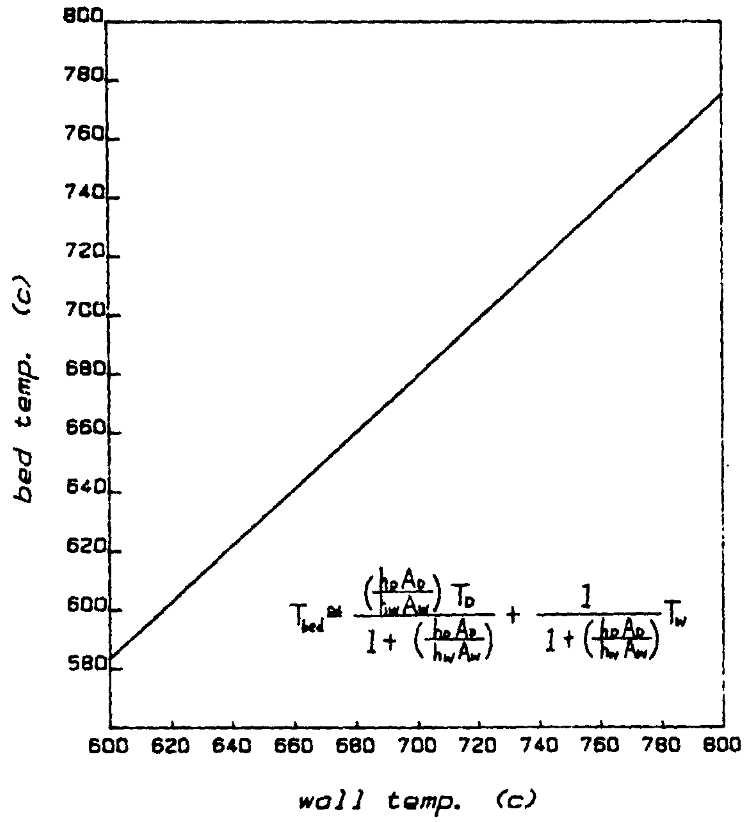
Kinetic parameters needed

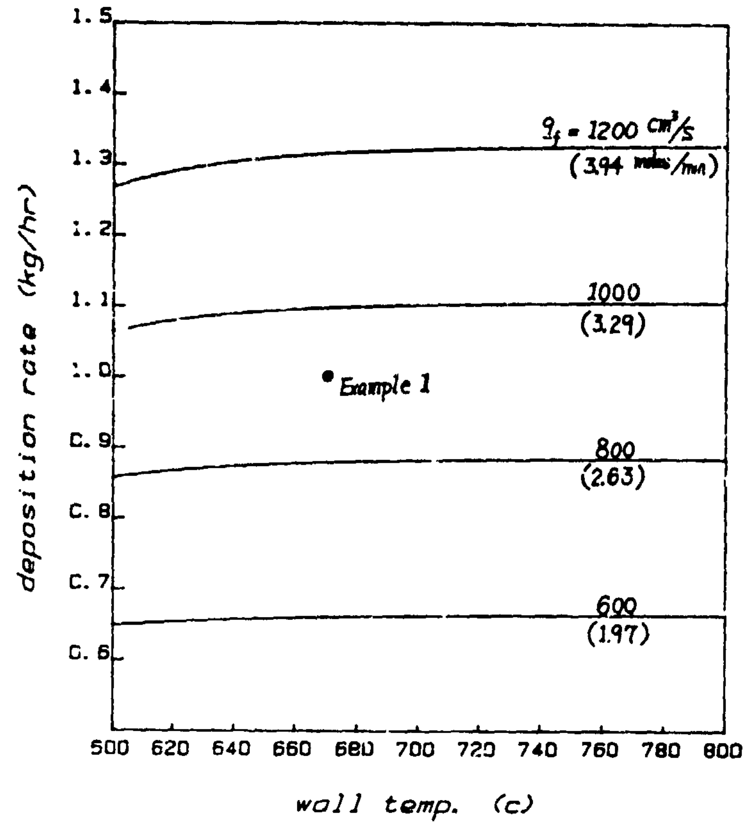
-	CVD growth rate	Iya et al. (1982)
-	homogeneous nucleation /reduction rate	

Particle interaction parameters needed

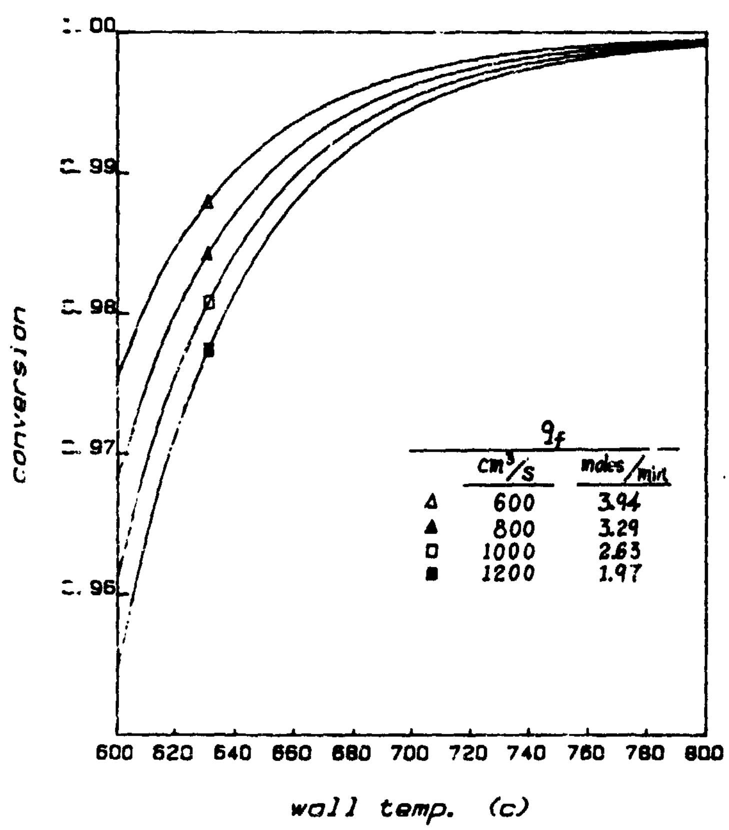
- coagulation coefficient for fines
- scavenging coefficient

CSTR — Batch Solids (20%)



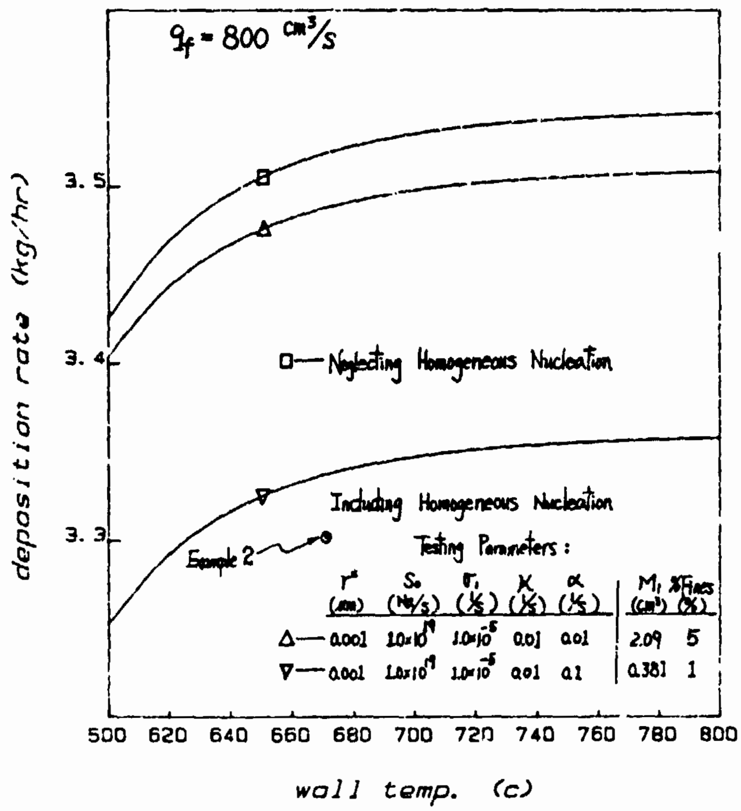


1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
deposition rate (kg/hr)
q_f = 1200 cm³/s
(3.94 moles/min)
1000
(3.29)
800
(2.63)
600
(1.97)
Example 1
500
620
640
660
680
700
720
740
760
780
800
wall temp. (c)



1.00
0.99
0.98
0.97
0.96
conversion
q_f
cm³/s
moles/min
600
3.94
800
3.29
1000
2.63
1200
1.97
600
620
640
660
680
700
720
740
760
780
800
wall temp. (c)

CSTR — Batch Solids (80%)



Bubbling Bed Model

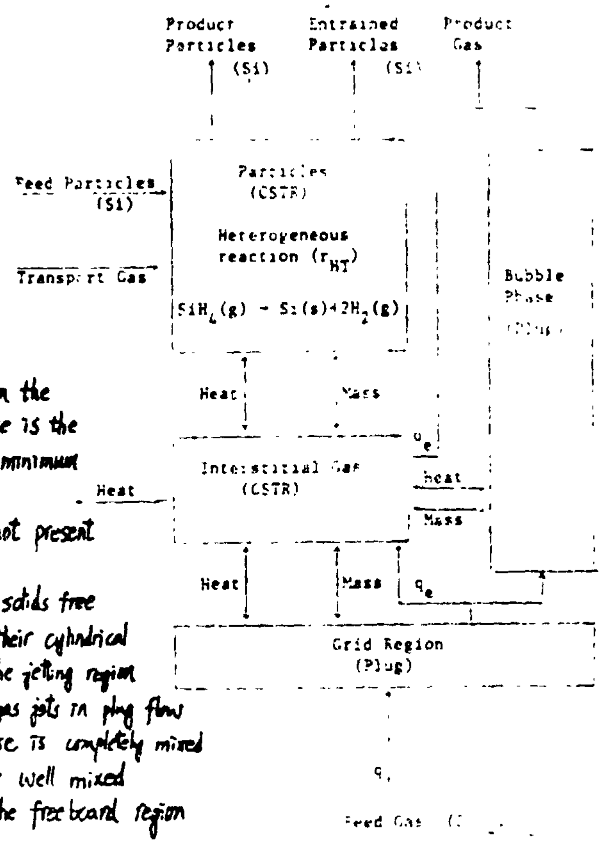


Figure 3.1. Modified two-phase model with ... nucleation

Assumptions:

1) The voidage in the emulsion phase is the same as at minimum fluidization
2) Particles are not present in bubbles
3) Gas jets are solids free and maintain their cylindrical shape within the jetting region
4. Bubbles and gas jets in plug flow
5. Emulsion phase is completely mixed
6. All solids are well mixed
7. Reaction in the freeboard region is ignored
8. Volumetric flow rate in the bubble and emulsion phase is const.
(9) Temp. of the particles is the same as the temp. of the emulsion phase.

<u>Bed parameters needed</u>

h_j - jet penetration depth		Yang and Keairns (1979)
$\bar{d}_b$ - average bubble diameter	}	We er and Clough (1981)
$\bar{\delta}_b$ - average volume fraction		
L_f - expanded bed height		
$\bar{U}_b$ - average bubble velocity		Kunii and Levenspiel (1969)
U_e - upward velocity of gas through the emulsion pha_e		ibis
$(K_{be})_b$, $(H_{be})_b$ - overall mass and heat transfer coefficient betwe the bubbles and the inte tal gas		ibis
K_{je}, H_{je} - overall mass and heat transfer coefficient between the jets and the interstitial g s		Weimer and Clough (1981)

h_w, h_d, L_{mf}, $K(R)$

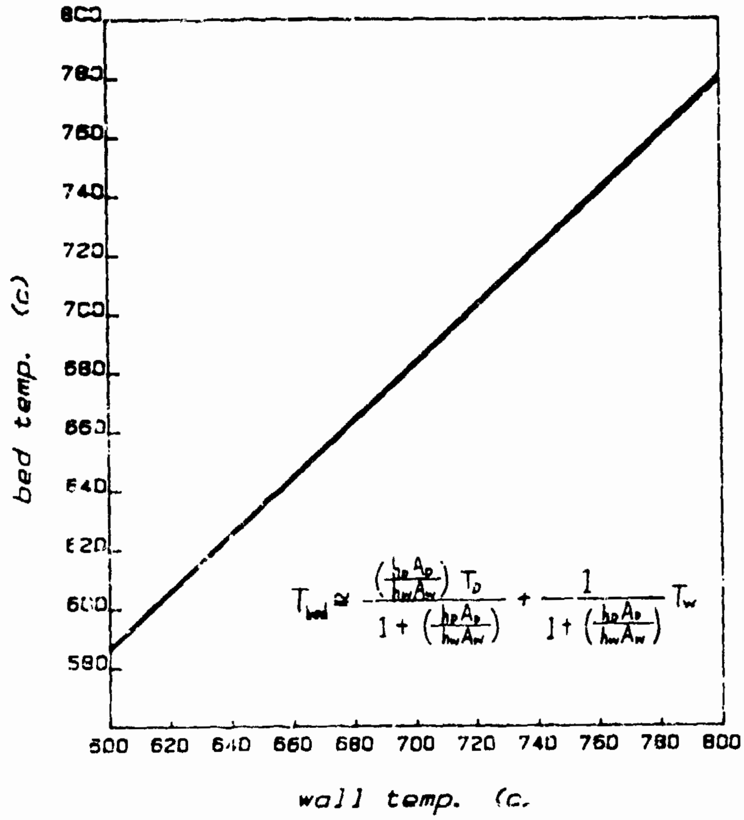
<u>Kinetic paramete.s needed</u>

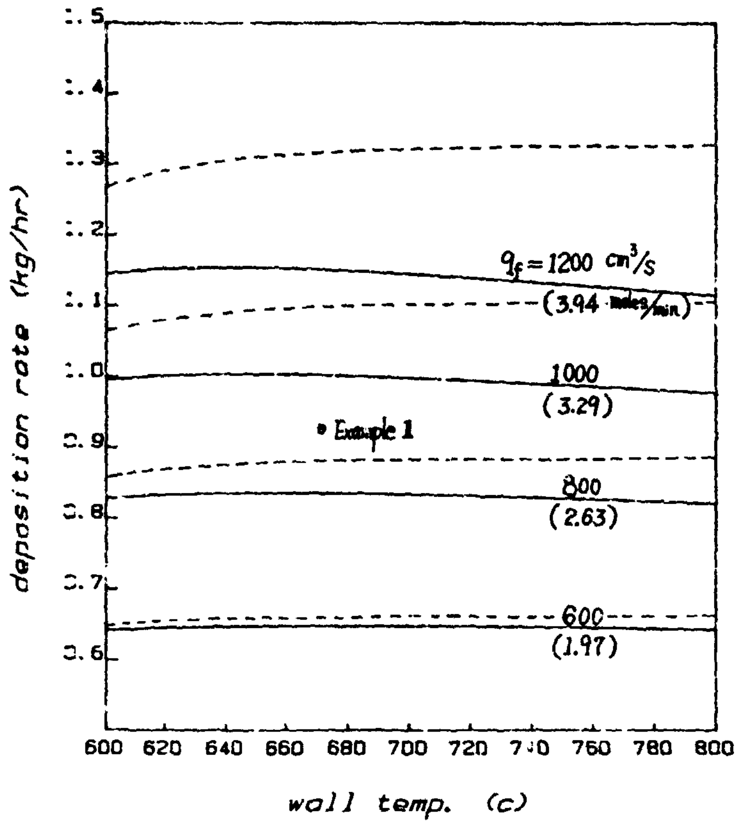
- CVD growth rate — Iya et al. (1982)
- homogeneous nucleation /reaction rate

<u>Particle interaction parameters needed</u>

- coagulation coefficient for fines
- scavenging coefficient

FBR — Batch Solids (20%)





----- CSTR Model Prediction
——— FBR Model Prediction

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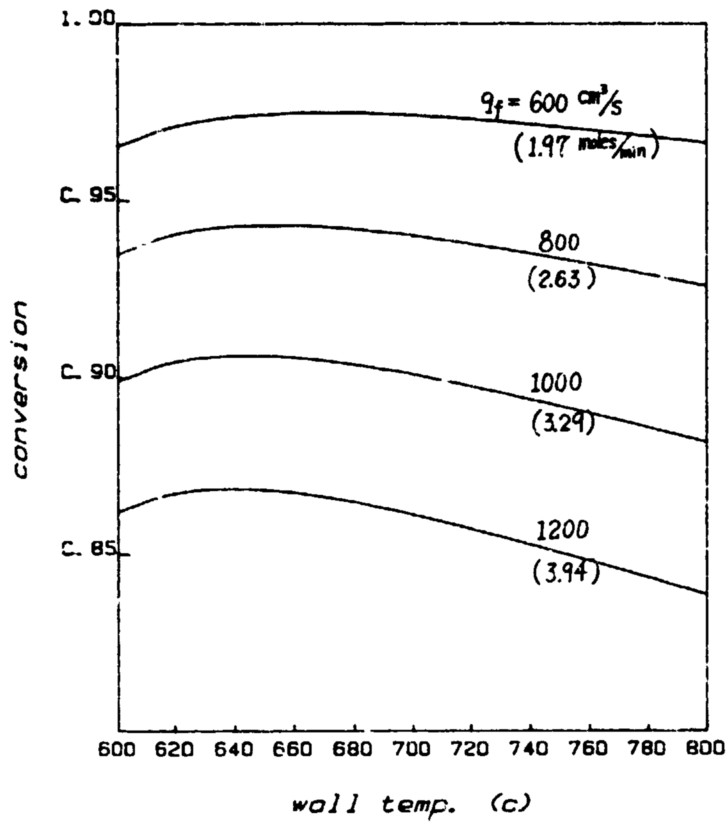

Selected Examples From JPL 6-in. FBR Experiments

	Silicon Seed		Experimental Conditions			
	Weight (Kg)	$\bar{d}_p$ (μm)	Silane Concen. (%)	Bed temp. (°C)	Total gas flow rate (moles/min)	Duration (min)
Example 1	10.50	227	20	650	3.0	90
Example 2	11.34	212	80	650	2.5	173

Product Comparison

	Experimental Data		Model Predicted (CSTR)		Model Predicted (FBR)	
	Production rate (Kg/hr)	$\bar{d}_p$ (μm)	Production rate (Kg/hr)	$\bar{d}_p$ (μm)	Production rate (Kg/hr)	$\bar{d}_p$ (μm)
Example 1	0.87	235.5	1.00	237.4	0.93	236.6
Example 2	3.50	241.5	3.35	260.3	3.16	257.7

Conclusion

— A preliminary comparison with two experimental results of JPL shows a reasonable agreement of model prediction with experiments.

— The deposition rate and conversion of silane are found to be lower for the two-phase fluidized bed model (FBR model) compared to the well-mixed reactor model (CSTR model). Only at low flowrates the performances from both model predictions are close.

— For the more general FBR model the deposition rate and conversion go through a slight maximum as the bed temperature is increased. Optimum Operating Conditions for the bed temperature and flowrate can be simulated by this model.

— The CSTR model which incorporates both homogeneous and heterogeneous reaction was developed to predict the generation, coagulation and scavenging of fines. Preliminary results show that the performance is very sensitive to the kinetic and interaction parameters. The results can be improved by using a more realistic FBR model and better estimates of parameters.