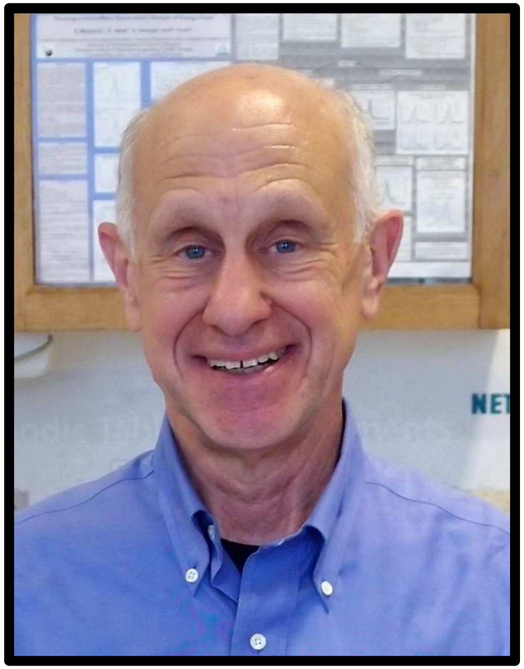
Soirée in the Museum of Fine Arts of Nancy, 9 May 2016

TOWARDS A REALISTIC KINETICS IN NON-ISOTHERMAL STUDIES

30 Years of a US – Hungarian Cooperation in Biomass Research



By Gábor Várhegyi

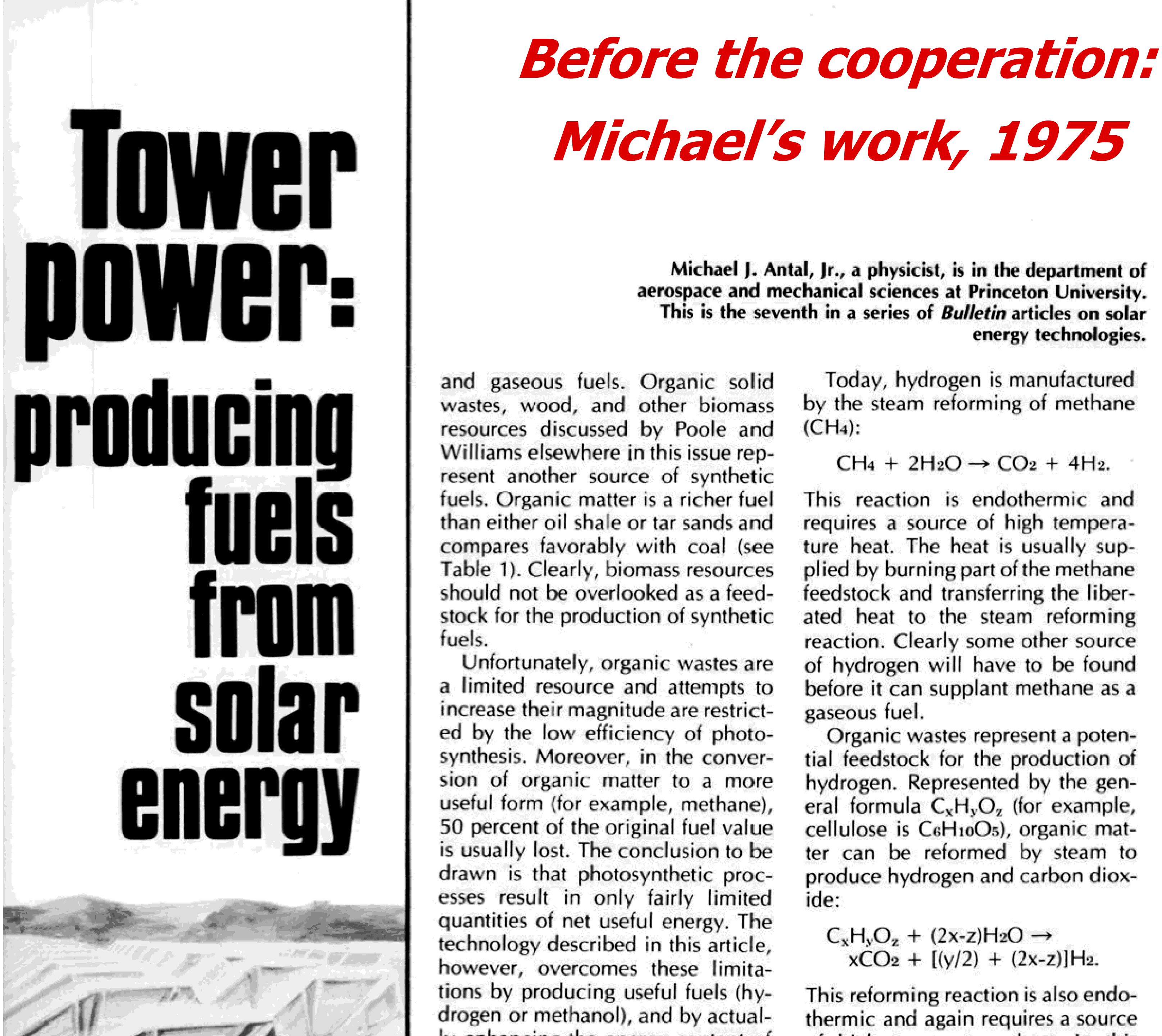
Institute of Materials and Environmental Chemistry,
Research Centre for Natural Sciences,
Hungarian Academy of Sciences

UNIVERSITY OF HAWAIʻI

mta ttk

Pyro 2016

Before the cooperation: Michael's work, 1975



Tower power: producing fuels from solar energy

Michael J. Antal, Jr., a physicist, is in the department of aerospace and mechanical sciences at Princeton University. This is the seventh in a series of *Bulletin* articles on solar energy technologies.

and gaseous fuels. Organic solid wastes, wood, and other biomass resources discussed by Poole and Williams elsewhere in this issue represent another source of synthetic fuels. Organic matter is a richer fuel than either oil shale or tar sands and compares favorably with coal (see Table 1). Clearly, biomass resources should not be overlooked as a feedstock for the production of synthetic fuels.

Unfortunately, organic wastes are a limited resource and attempts to increase their magnitude are restricted by the low efficiency of photosynthesis. Moreover, in the conversion of organic matter to a more useful form (for example, methane), 50 percent of the original fuel value is usually lost. The conclusion to be drawn is that photosynthetic processes result in only fairly limited quantities of net useful energy. The technology described in this article, however, overcomes these limitations by producing useful fuels (hydrogen or methanol), and by actual-

Today, hydrogen is manufactured by the steam reforming of methane (CH_4):

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2.$$

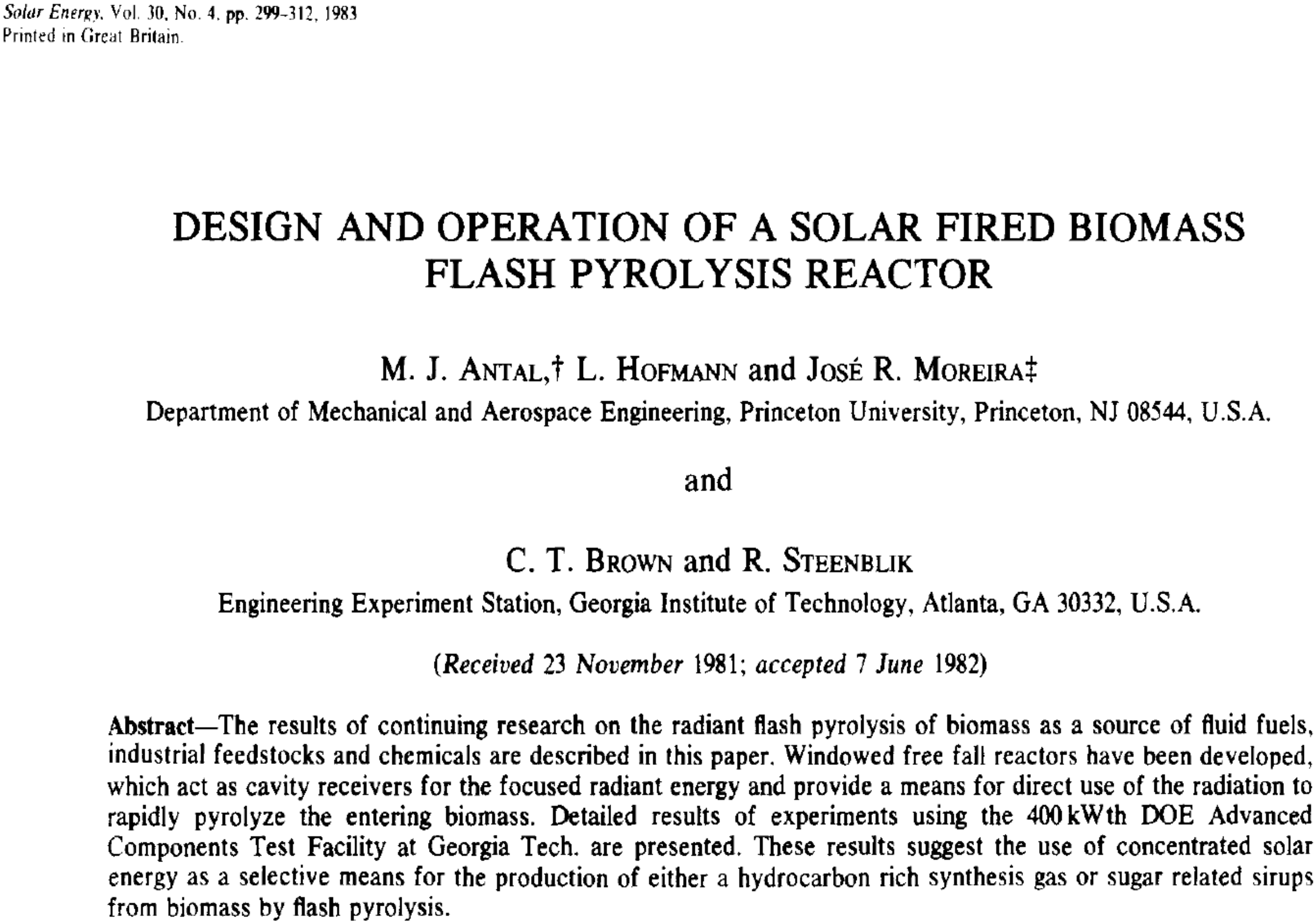
This reaction is endothermic and requires a source of high temperature heat. The heat is usually supplied by burning part of the methane feedstock and transferring the liberated heat to the steam reforming reaction. Clearly some other source of hydrogen will have to be found before it can supplant methane as a gaseous fuel.

Organic wastes represent a potential feedstock for the production of hydrogen. Represented by the general formula $C_xH_yO_z$ (for example, cellulose is $C_6H_{10}O_5$), organic matter can be reformed by steam to produce hydrogen and carbon dioxide:

$$C_xH_yO_z + (2x\text{-}z)H_2O \rightarrow xCO_2 + [(y/2) + (2x\text{-}z)]H_2.$$

This reforming reaction is also endothermic and again requires a source

Before the cooperation: Michael's work, 1983



Solar Energy, Vol. 30, No. 4, pp. 299–312, 1983
Printed in Great Britain.

DESIGN AND OPERATION OF A SOLAR FIRED BIOMASS FLASH PYROLYSIS REACTOR

M. J. Antal,† L. Hofmann and José R. Moreira‡
Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544, U.S.A.

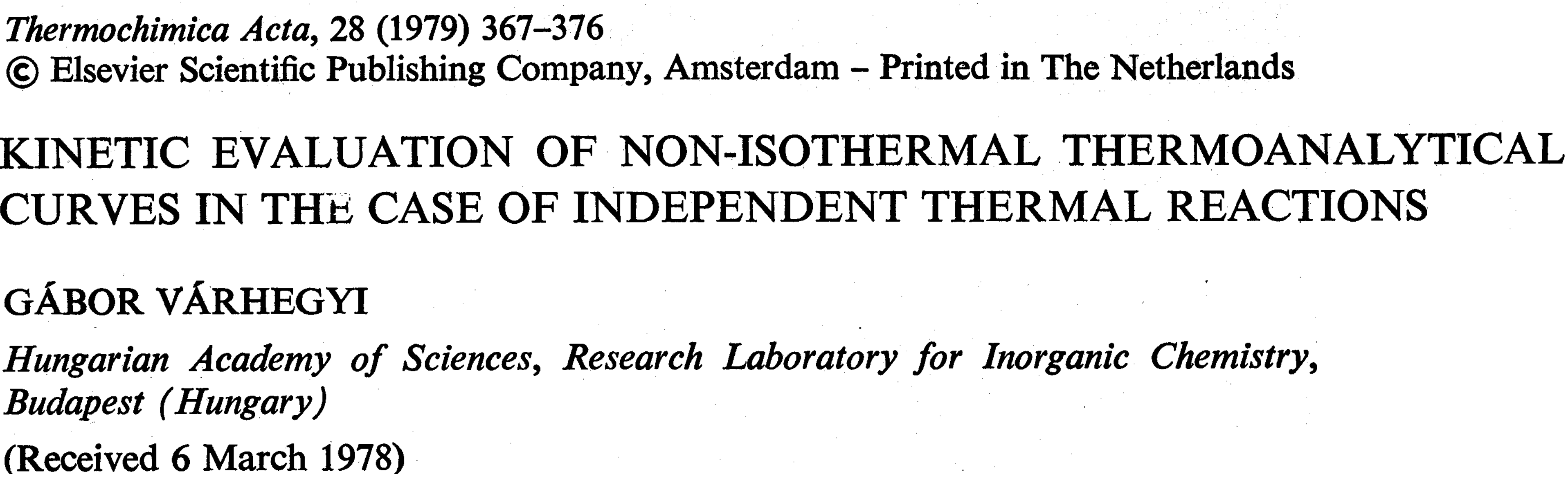
and

C. T. Brown and R. Steenblik
Engineering Experiment Station, Georgia Institute of Technology, Atlanta, GA 30332, U.S.A.

(*Received* 23 *November* 1981; *accepted* 7 *June* 1982)

Abstract—The results of continuing research on the radiant flash pyrolysis of biomass as a source of fluid fuels, industrial feedstocks and chemicals are described in this paper. Windowed free fall reactors have been developed, which act as cavity receivers for the focused radiant energy and provide a means for direct use of the radiation to rapidly pyrolyze the entering biomass. Detailed results of experiments using the 400 kWth DOE Advanced Components Test Facility at Georgia Tech. are presented. These results suggest the use of concentrated solar energy as a selective means for the production of either a hydrocarbon rich synthesis gas or sugar related sirups from biomass by flash pyrolysis.

Before the cooperation: my work, 1978



Thermochimica Acta, 28 (1979) 367–376
© Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

KINETIC EVALUATION OF NON-ISOTHERMAL THERMOANALYTICAL CURVES IN THE CASE OF INDEPENDENT THERMAL REACTIONS

GÁBOR VÁRHEGYI

Hungarian Academy of Sciences, Research Laboratory for Inorganic Chemistry, Budapest (Hungary)

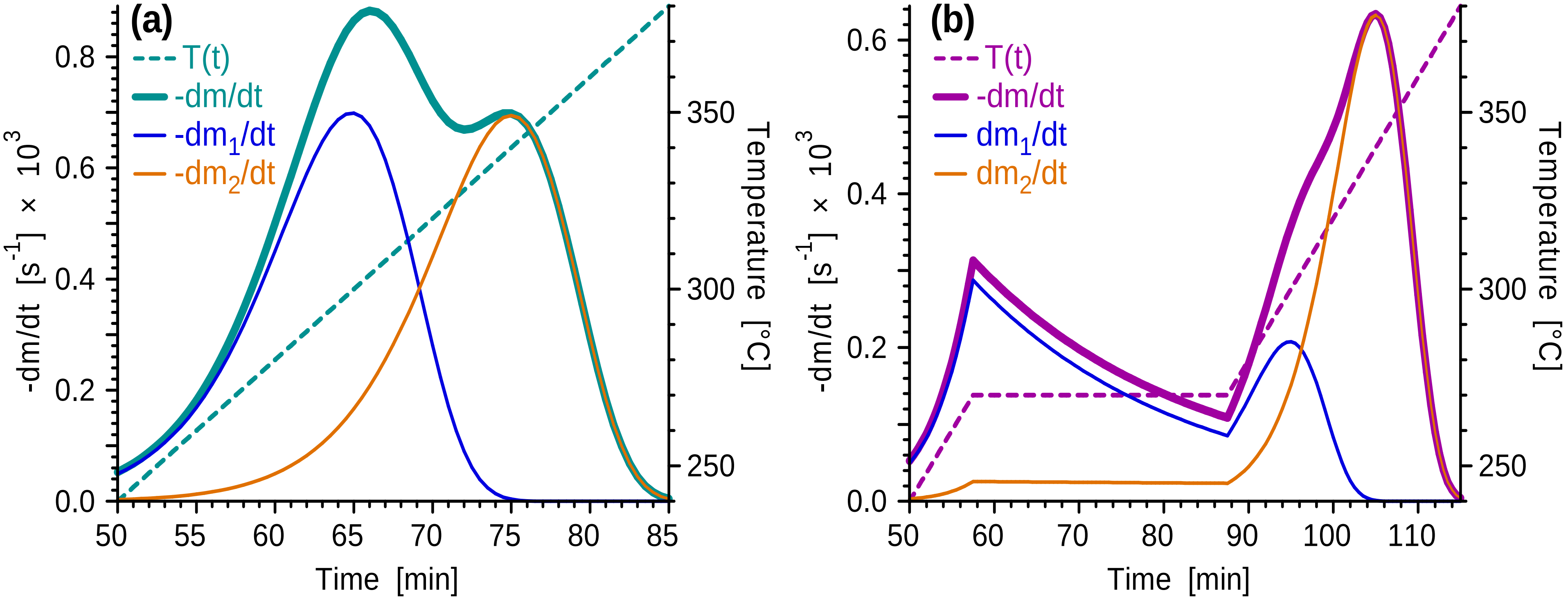
(Received 6 March 1978)

Simultaneous evaluation of a series of experiments by the method of least squares:

$$S_X = \sum_m \sum_i [X_m^{obs}(t_i) - X_m^{calc}(t_i)]^2$$

In later works, from 1992, the $X_m^{obs}(t_i) - X_m^{calc}(t_i)$ differences were normalized to compensate the different magnitudes of the experiments and the different number of digitized points on the curves.

Before the cooperation: my work, 1978

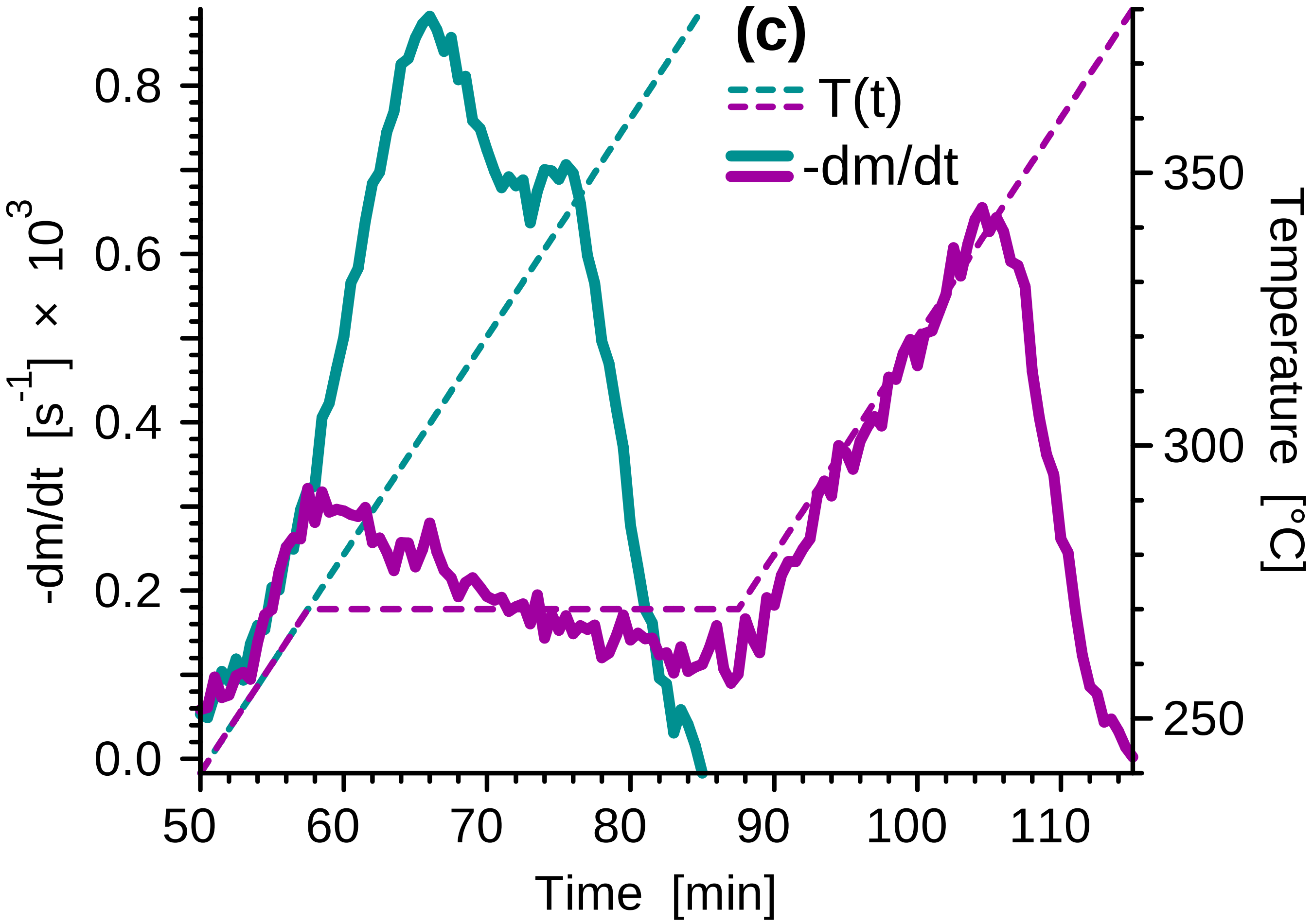


Construction of simulated experiments for test evaluations at **linear heating (left)** and at a **stepwise heating (right)**.

The **blue** and **orange** lines represent the mass loss rate of first order reactions. The thick solid lines (— , —) are the sums of the blue and the orange curves.

(The above figures were reconstructed from the parameters published in 1978.)

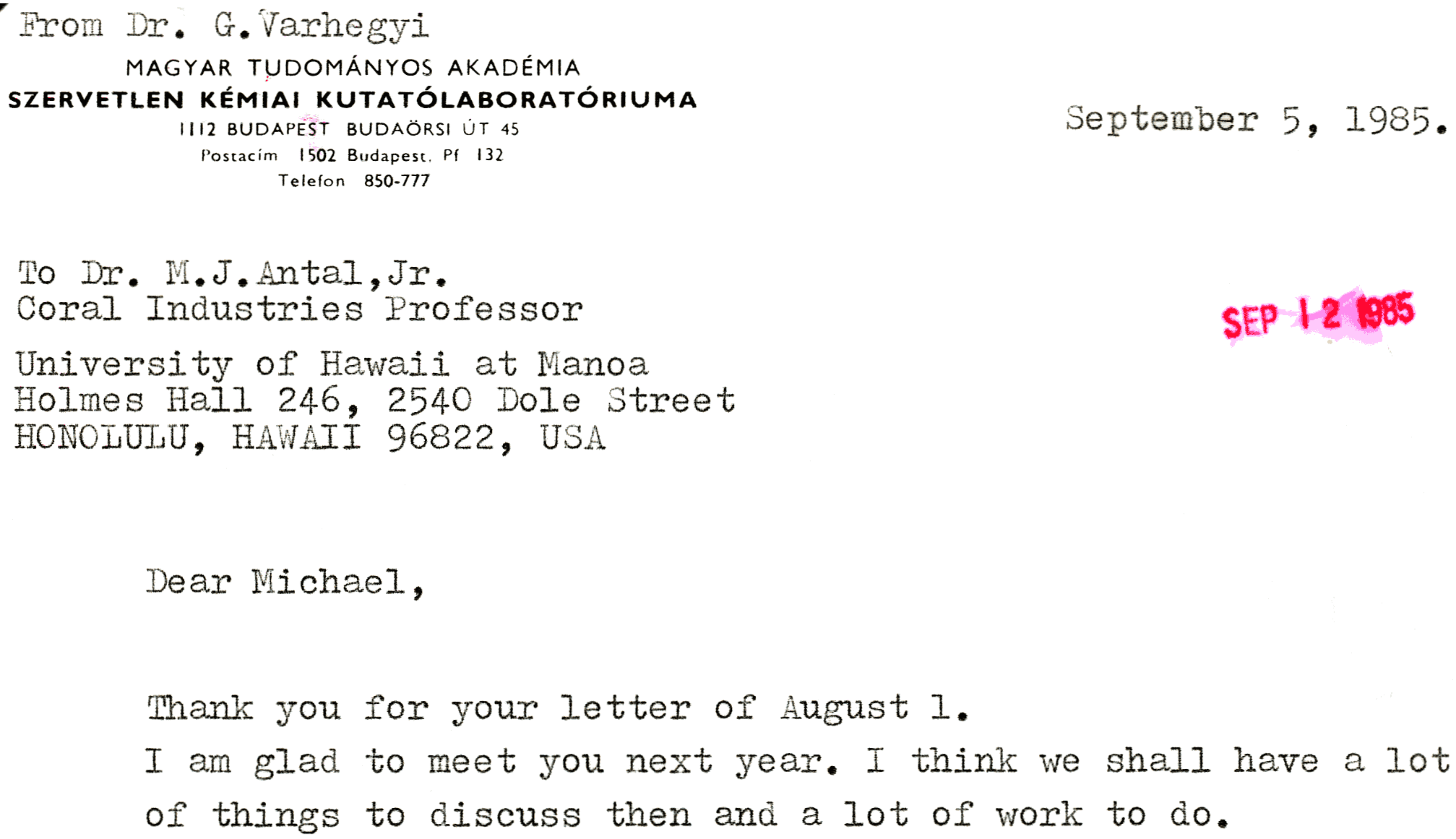
Before the cooperation: my work, 1978



Simultaneous least squares evaluation of “experiments” simulated at **linear** and **stepwise** heating. (A Gaussian noise of $\sigma = 1.67 \times 10^{-3}$ s^{-1} was added to the –dm/dt curves shown in the previous slide.)

(This figure was reconstructed from the parameters published in 1978.)

September 1985: Letter to Michael



From Dr. G.Varhegyi
MAGYAR TUDOMÁNYOS AKADÉMIA
SZERVETLEN KÉMIAI KUTATÓLABORATÓRIUMA
1112 BUDAPEST BUDAÖRSI ÚT 45
Postacím 1502 Budapest, Pf 132
Telefon 850-777

September 5, 1985.

To Dr. M.J.Antal,Jr.
Coral Industries Professor

University of Hawaii at Manoa
Holmes Hall 246, 2540 Dole Street
HONOLULU, HAWAII 96822, USA

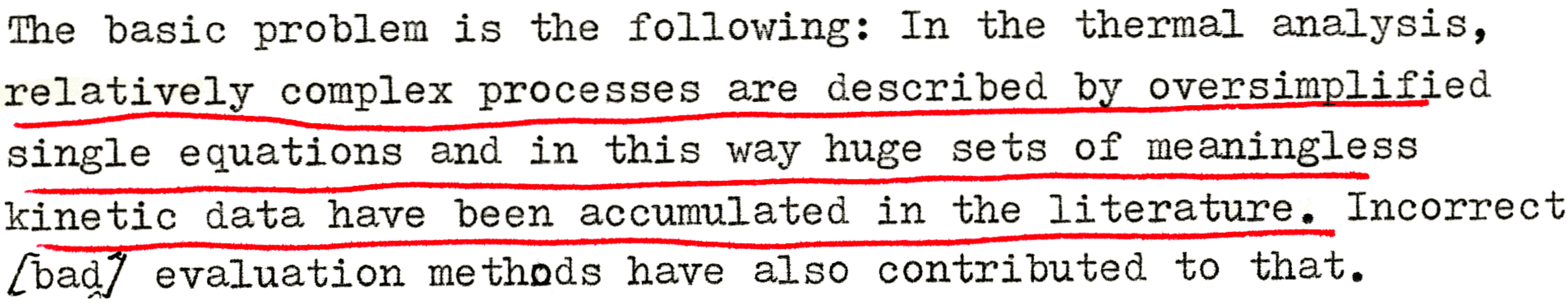
SEP 12 1985

Dear Michael,

Thank you for your letter of August 1.
I am glad to meet you next year. I think we shall have a lot of things to discuss then and a lot of work to do.

September 1985: Letter to Michael

(He marked a sentence by red underline when he read it)



The basic problem is the following: In the thermal analysis, relatively complex processes are described by oversimplified single equations and in this way huge sets of meaningless kinetic data have been accumulated in the literature. Incorrect [bad] evaluation methods have also contributed to that.

The text with larger letters :

The basic problem is the following: In the thermal analysis, relatively complex processes are described by oversimplified single equations, and in this way huge sets of meaningless kinetic data have been accumulated in the literature. Incorrect [bad] evaluation methods have also contributed to that.

Next summer (1986) in Budapest:

Back row: Michael, a technician, and I.

Front row:
Dr. Piroska Szabó and Dr. Emma Jakab, who were important participants in this cooperation.*

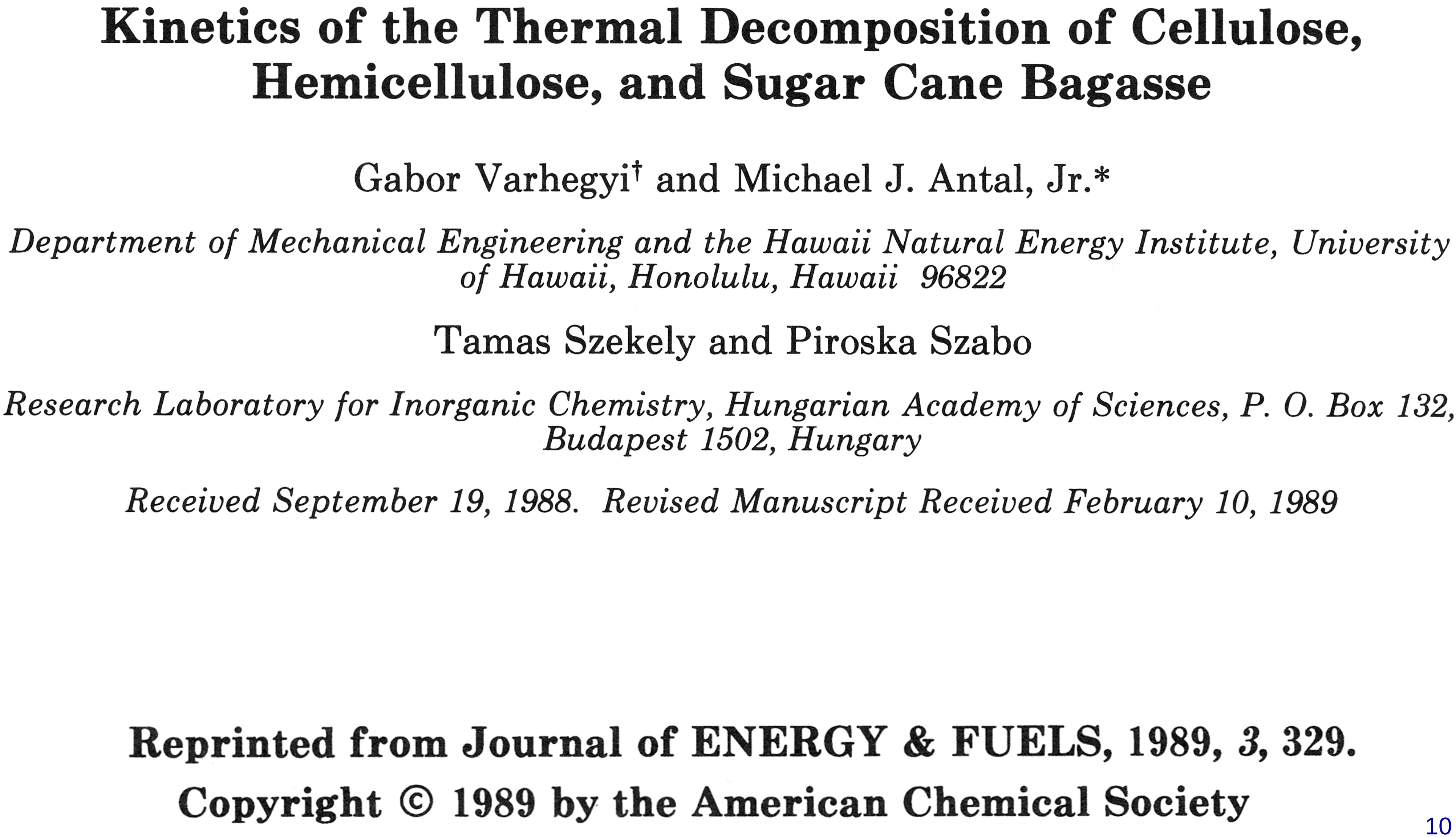
Background: The mass spectrometer and the computer of a TGA-MS system.

---

*See the **Acknowledgment** at the end for a list of 15 participating colleagues.

This photo was published in:
G. Várhegyi, Energy Fuels 2016, 30, doi: 10.1021/acs.energyfuels.6b00860

The first common work on non-isothermal kinetics, 1989:



Kinetics of the Thermal Decomposition of Cellulose, Hemicellulose, and Sugar Cane Bagasse

Gabor Varhegyi[†] and Michael J. Antal, Jr.*

Department of Mechanical Engineering and the Hawaii Natural Energy Institute, University of Hawaii, Honolulu, Hawaii 96822

Tamas Szekely and Piroska Szabo

Research Laboratory for Inorganic Chemistry, Hungarian Academy of Sciences, P. O. Box 132, Budapest 1502, Hungary

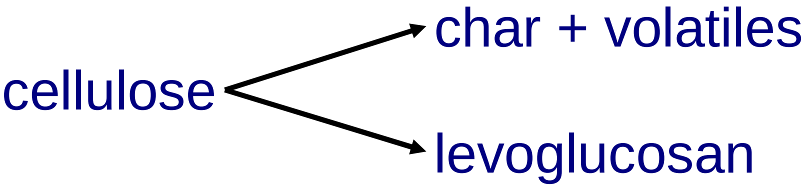
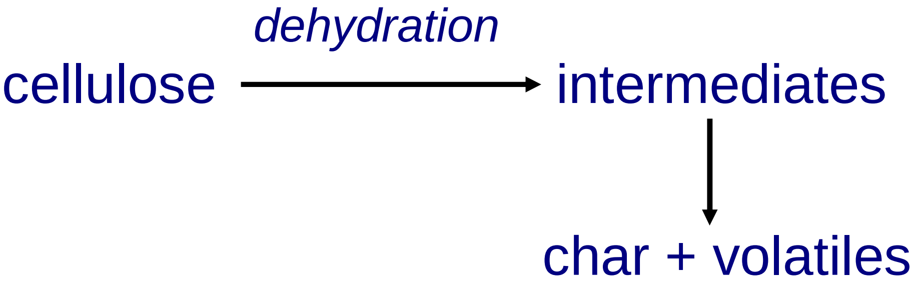
Received September 19, 1988. Revised Manuscript Received February 10, 1989

Reprinted from Journal of ENERGY & FUELS, 1989, *3*, 329.

The first common work on non-isothermal kinetics, 1989:

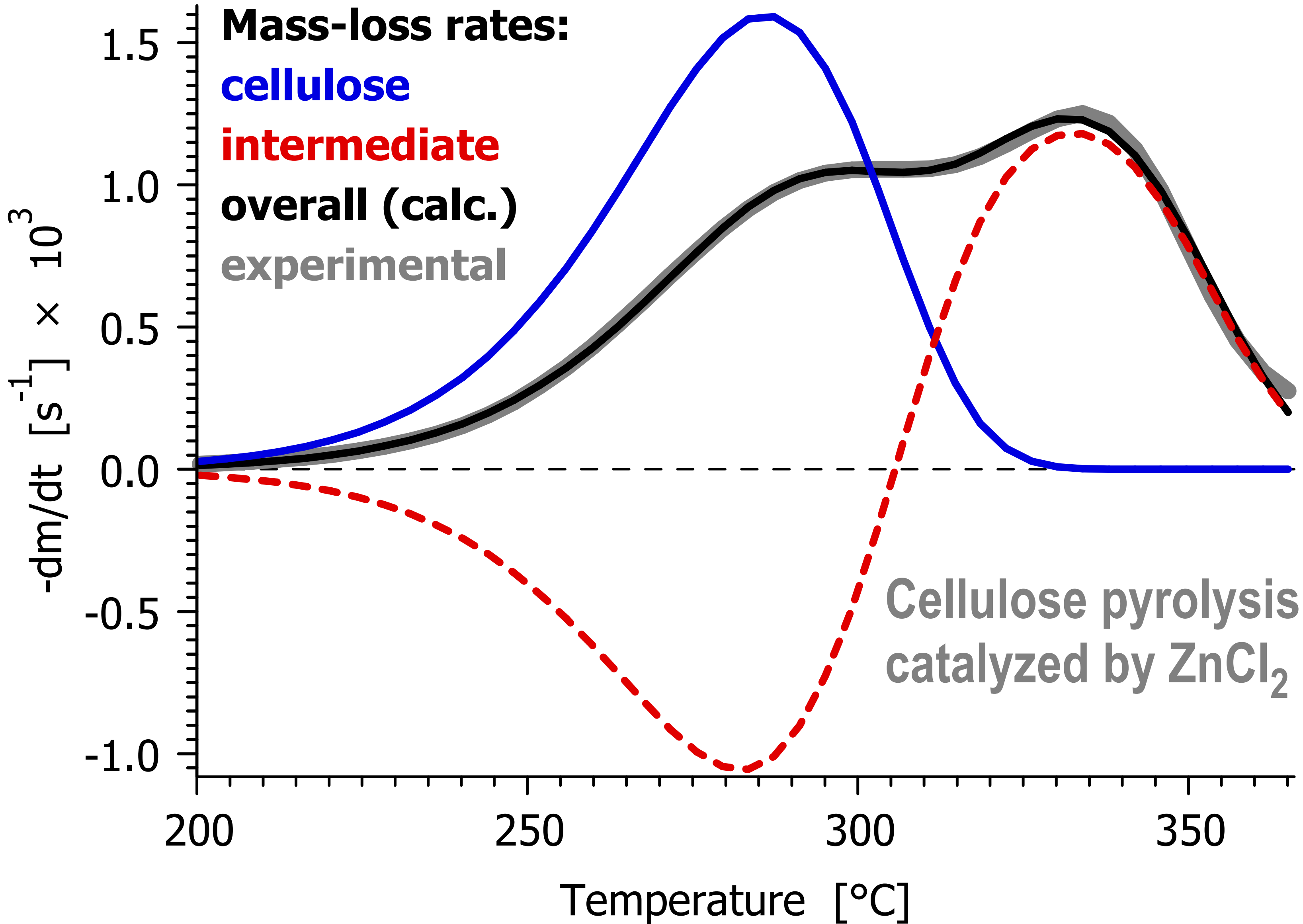
The studied models included: **(i)** Parallel reactions; **(ii)** Competitive reactions; **(iii)** Successive reactions; **(iv)** Combination of parallel and successive reactions.

Examples: Cellulose in the presence of inorganic compounds (one cation per 100 monomer units)

Competitive reactions (NaCl):	Successive reactions ($ZnCl_2$):
 cellulose char + volatiles levoglucosan	 *dehydration* cellulose intermediates char + volatiles

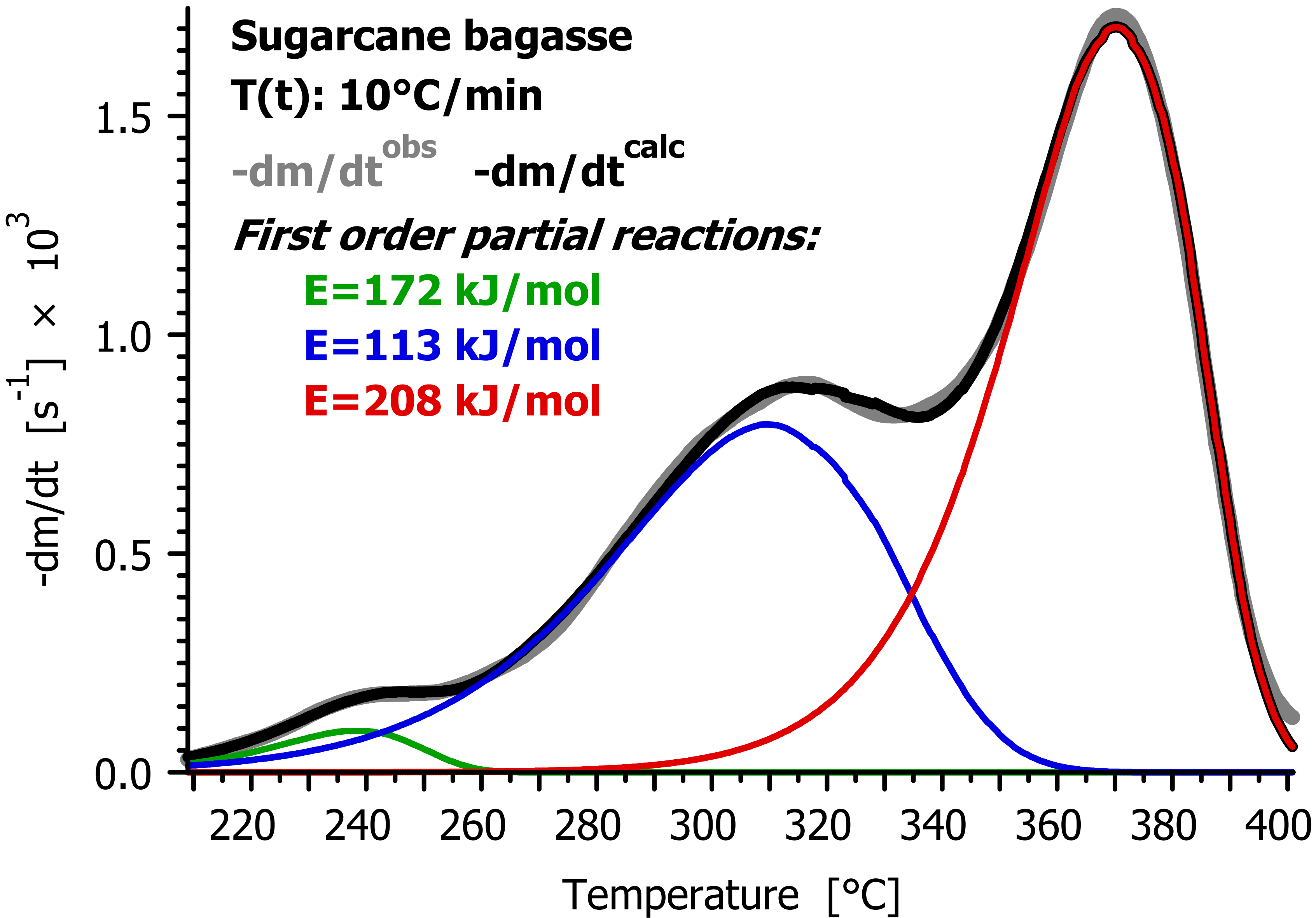
1989: Pyrolysis of cellulose catalyzed by $ZnCl_2$

Cellulose $\longrightarrow$ **intermediate** + H_2O + … $\longrightarrow$ **char** + …



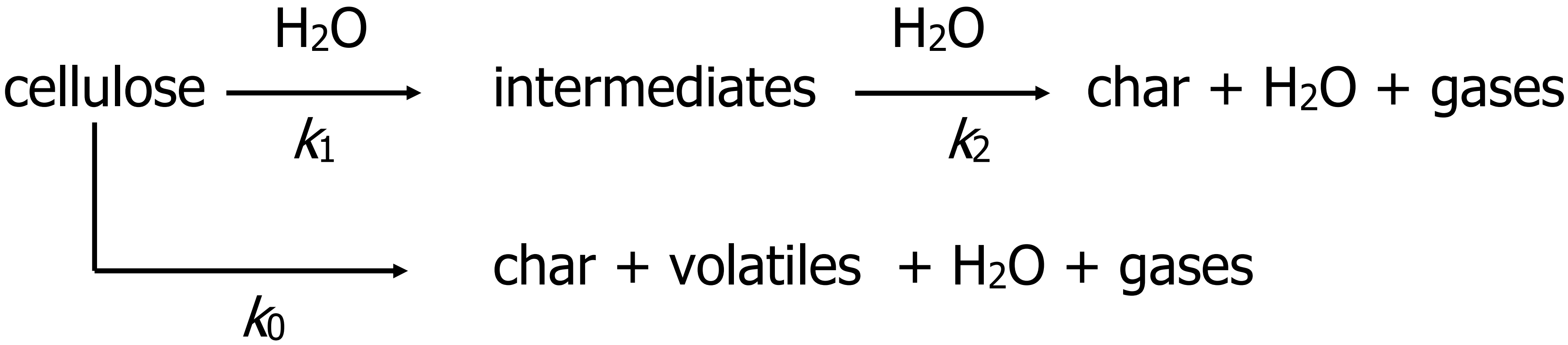
1989: Pyrolysis of bagasse

3 parallel 1st order reactions (= 3 pseudocomponents)



1993: A complex autocatalytic reaction scheme and the simultaneous evaluation of a series of experiments by the method of least squares

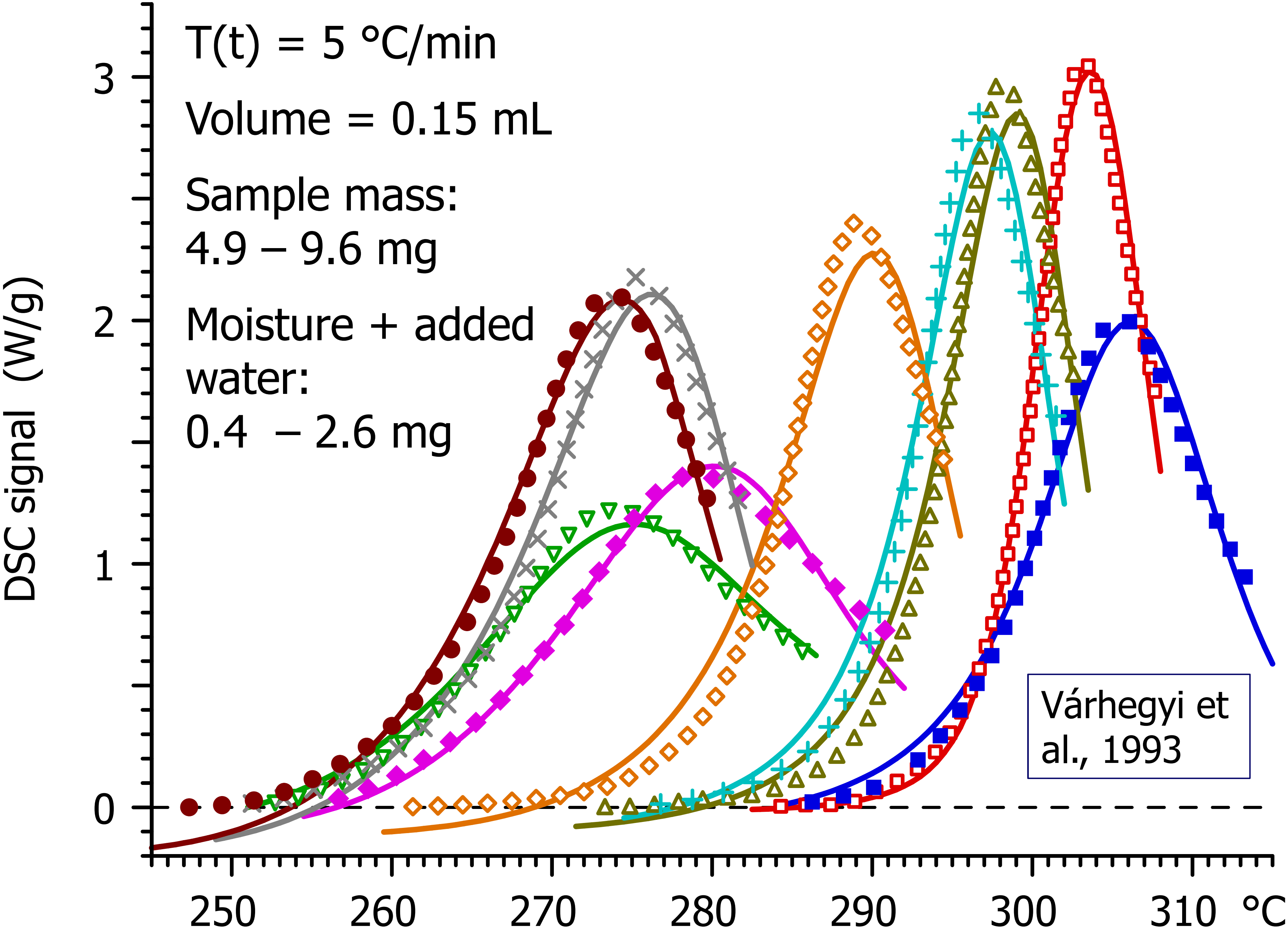
Thermal decomposition of cellulose in closed sample holder. The water, which is a main volatile product, catalyzes the decomposition:



$$\begin{tikzcd}
\text{cellulose} \arrow[r, "H_2O", "k_1"'] \arrow[dr, "k_0"'] & \text{intermediates} \arrow[r, "H_2O", "k_2"'] & \text{char} + H_2O + \text{gases} \\
& \text{char} + \text{volatiles} + H_2O + \text{gases} &
\end{tikzcd}$$

Várhegyi, G.; Szabó, P.; Mok W. S. L., Antal, M. J., Jr.: Kinetics of the thermal decomposition of cellulose in sealed vessels at elevated pressures. Effects of the presence of water on the reaction mechanism. *J. Anal. Appl. Pyrolysis* **1993**, *26*, 159-174.

Least squares evaluation of a series of experiments:



T(t) = 5 °C/min

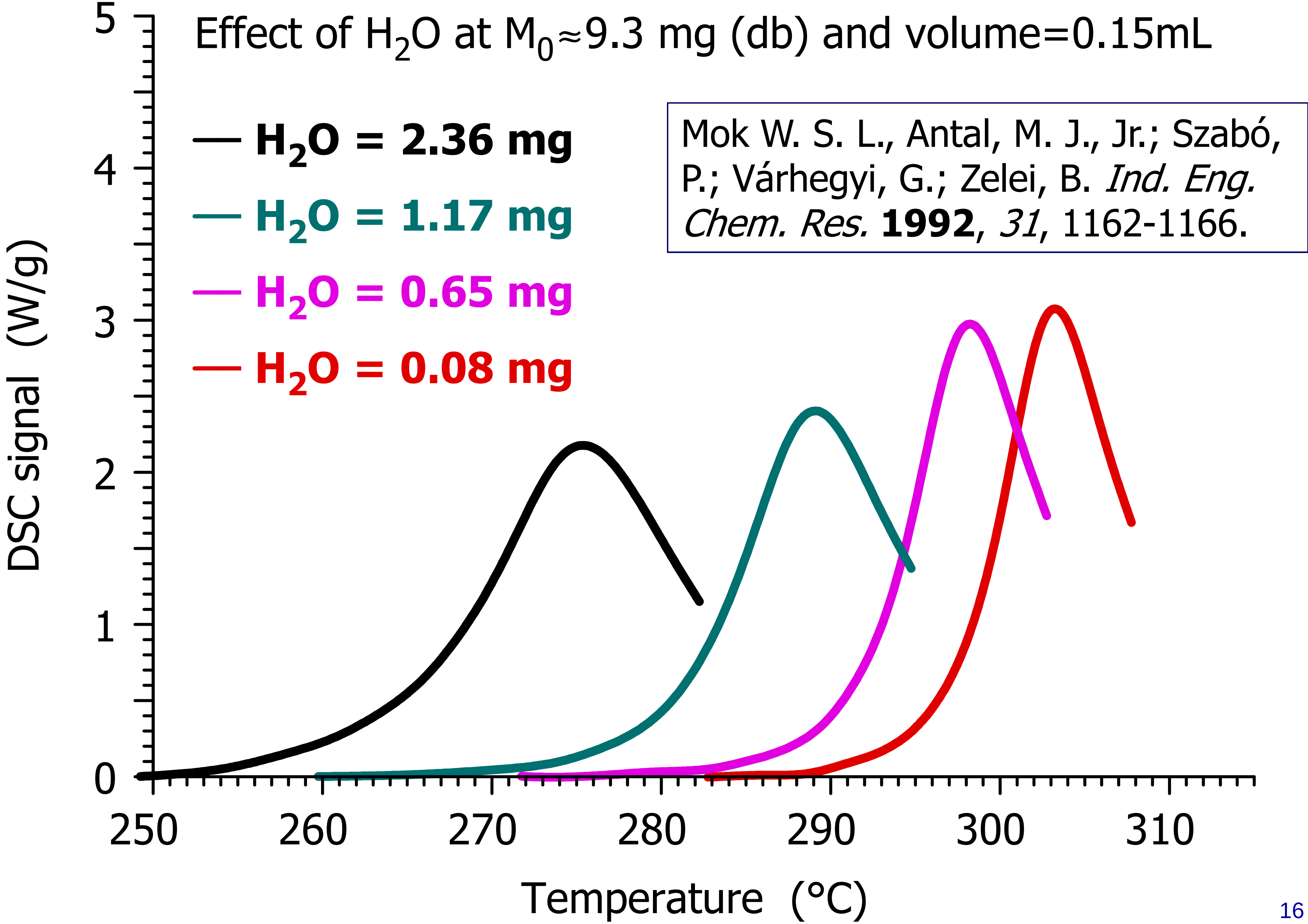
Volume = 0.15 mL

Sample mass:
4.9 – 9.6 mg

Moisture + added water:
0.4 – 2.6 mg

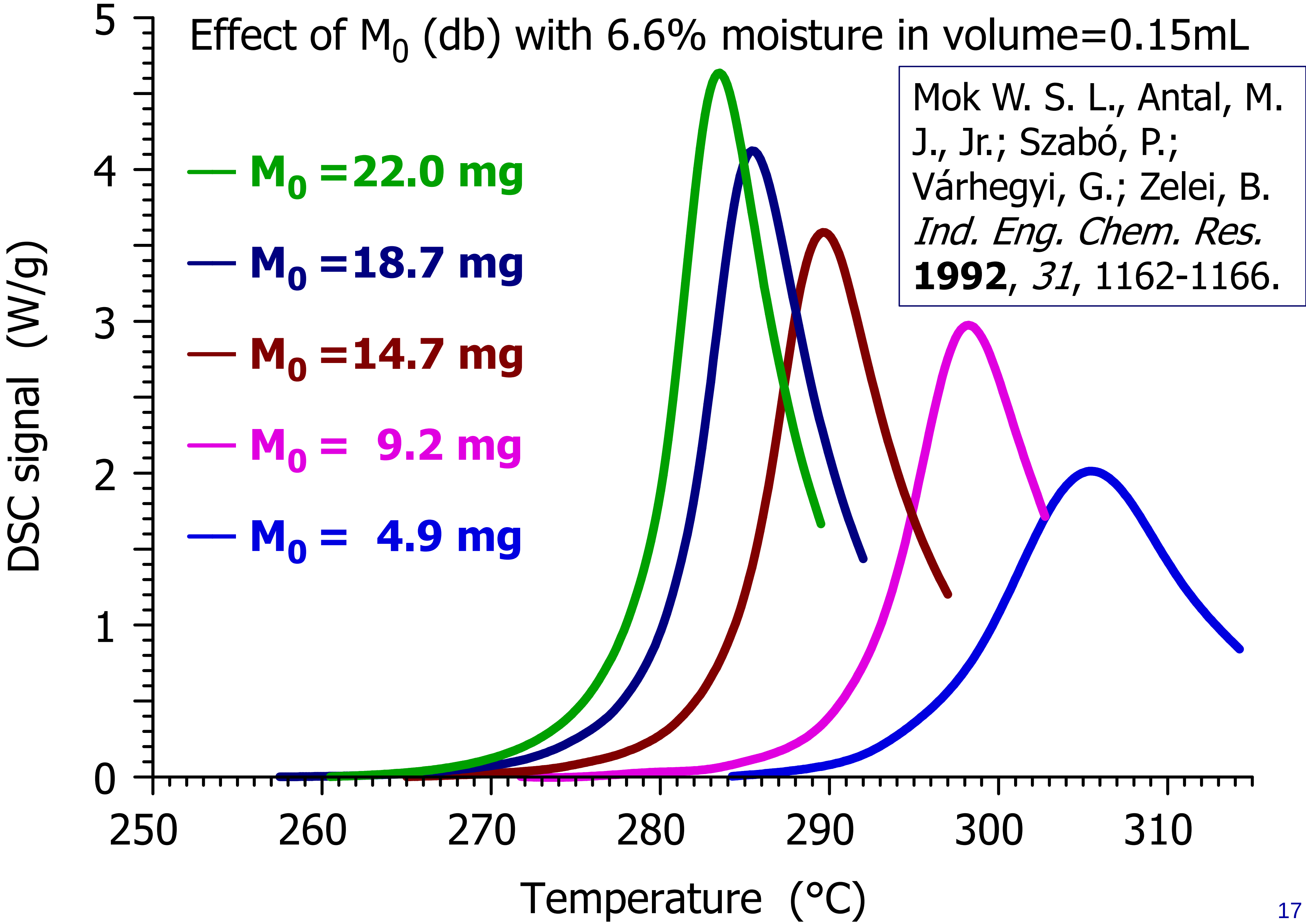
Várhegyi et al., 1993

These were the effects modelled, 1: (1992)



Mok W. S. L., Antal, M. J., Jr.; Szabó, P.; Várhegyi, G.; Zelei, B. *Ind. Eng. Chem. Res.* **1992**, *31*, 1162-1166.

These were the effects modelled, 2: (1992)



Mok W. S. L., Antal, M. J., Jr.; Szabó, P.; Várhegyi, G.; Zelei, B. *Ind. Eng. Chem. Res.* **1992**, *31*, 1162-1166.

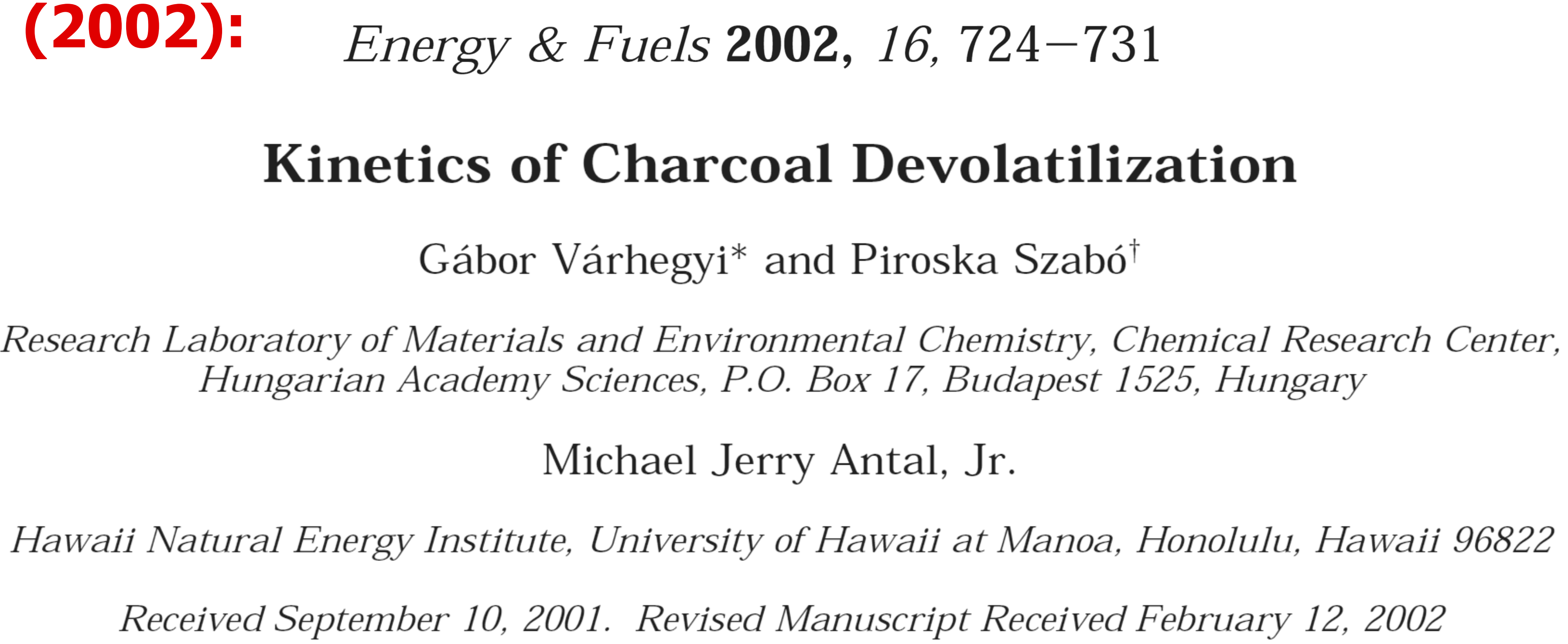
Least squares evaluation of a series of experiments (1993):

Várhegyi et al., 1993

$$of = \sum_{k=1}^{N_{exper}} \sum_{i=1}^{N_{points}} \frac{\left[X_k^{obs}(t_i) - X_k^{calc}(t_i)\right]^2}{N_{points} h_k^2}$$

Here X_k^{obs} is an experimental quantity (DSC signal) normalized by the initial sample mass. Subscript k distinguishes the experiments evaluated together. X_k^{calc} denotes the predicted values of the kth experimental curve which is obtained by the numerical solution of the kinetic equation at each iteration step. N_{points} denotes the number of t_i time points at which a digitized value is available. N_{exper} is the number of experimental curves evaluated together. h_k is the highest point of the given experimental curve; this normalization serves to counterbalance the magnitude differences.

Kinetics of a complicated devolatilization process (2002):



Energy & Fuels **2002**, *16*, 724−731

Kinetics of Charcoal Devolatilization

Gábor Várhegyi* and Piroska Szabó†

Research Laboratory of Materials and Environmental Chemistry, Chemical Research Center, Hungarian Academy Sciences, P.O. Box 17, Budapest 1525, Hungary

Michael Jerry Antal, Jr.

Hawaii Natural Energy Institute, University of Hawaii at Manoa, Honolulu, Hawaii 96822

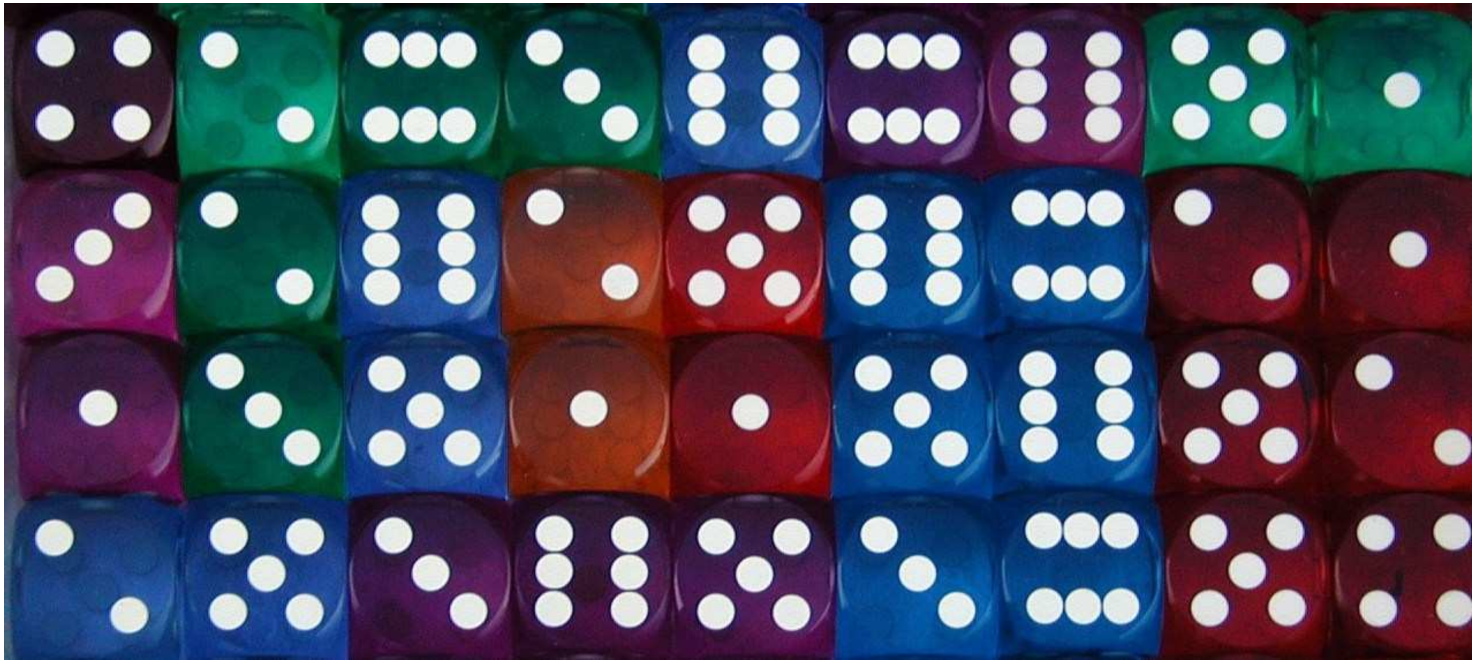
Received September 10, 2001. Revised Manuscript Received February 12, 2002

A high-temperature heat treatment of the charcoals serves to produce valuable biocarbons that have good electrical conductivity.

The chemistry of the devolatilization is not simple. A charcoal formed below 500°C contains a wide variety of chemical structures built from carbon, oxygen (ca. 20% of the charcoal), hydrogen, and (occasionally) nitrogen.

A distributional approach (Vand 1943, Pitt 1962, Anthony and Howard 1976)

- There is a huge number of elementary reactions during the pyrolysis of most organic samples
- The problem is similar to the mechanics of the molecules in physics: if we have many molecules in a system, we cannot write up the Newtonian equations for each; instead of that one can employ statistical mechanics ...



A distributional approach (Vand 1943, Pitt 1962, Anthony and Howard 1976), continued

- Organic samples usually contain many different pyrolyzing species.

  (Even the same chemical species may have differing reactivity if their pyrolysis is influenced by other species in their vicinity.)

- *A simplification:* On a molecular level we assume that each species undergoes a first-order decay.

- The reactivity differences are described by different activation energy values.

- A distribution function is assumed for the activation energies to keep the number of the (unknown) model parameters at a reasonable level.

Kinetics of charcoal devolatilization (2002):

- TGA-MS experiments were evaluated;
- More than one DAEM was assumed because the charcoal devolatilization takes place in very wide temperature domain where different type of reactions occur (as the TGA-MS curves indicated);

  A single DAEM was enough for the observed intensities of CH_3^+, $C_2H_3^+$, and $C_2H_5^+$. Two parallel DAEMs were needed for the double peak of the H_2^+ intensity. Four DAEMs were needed for the description of the overall –dm/dt curve.

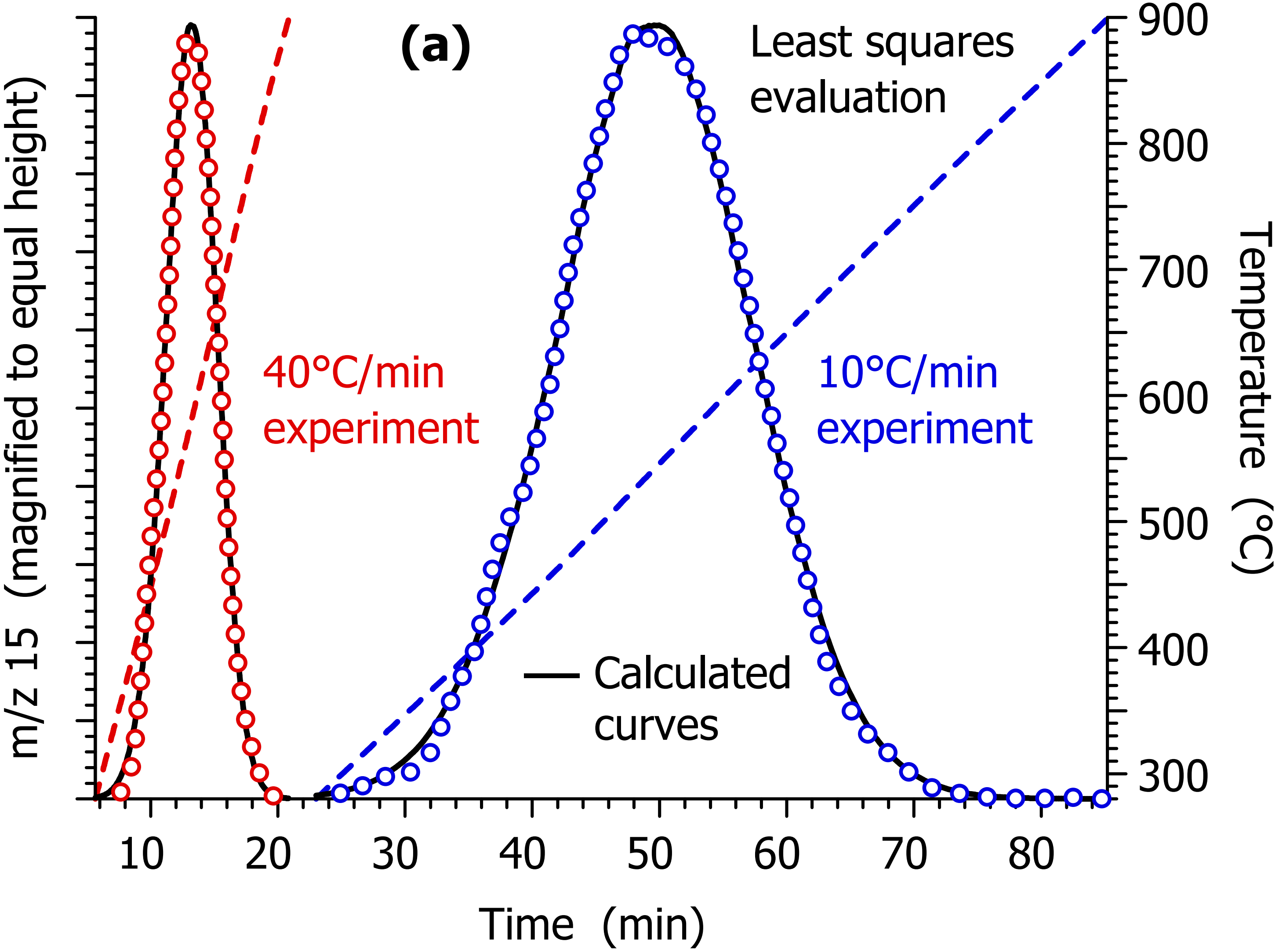
- The evaluation was based on more than one experiment.
- The series of experiments evaluated together included linear and stepwise T(t) programs;

Kinetics of charcoal devolatilization (2002), *continued*

- The method of the least squares was employed;
- The DAEMs were solved numerically along the given T(t) functions at each set of parameters that arose during the minimization of the least squares sum by the parameters.

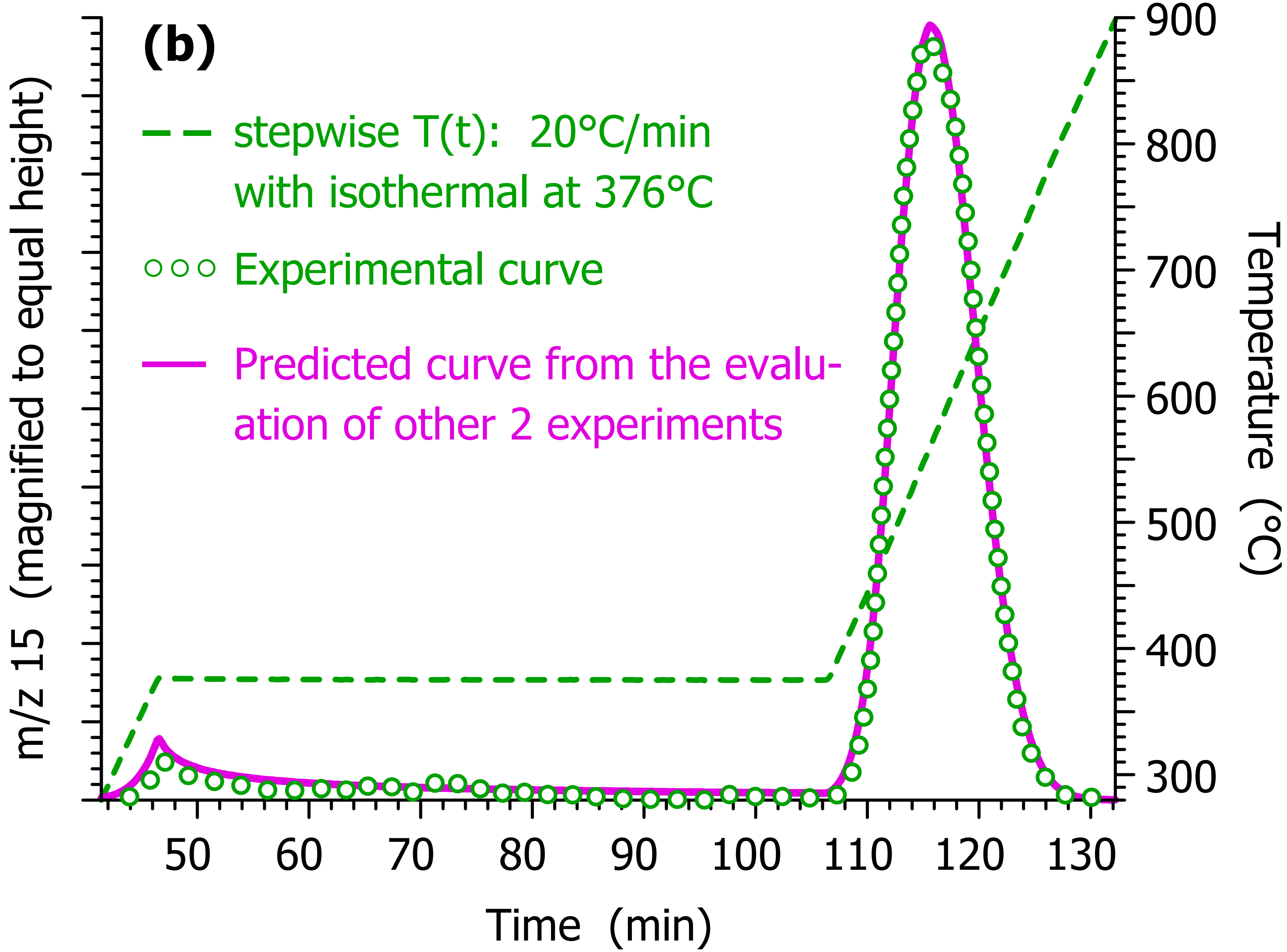
  A high-precision numerical method was employed which was freshly published that times by Donskoi and McElwain.

A simple prediction test, 2002:



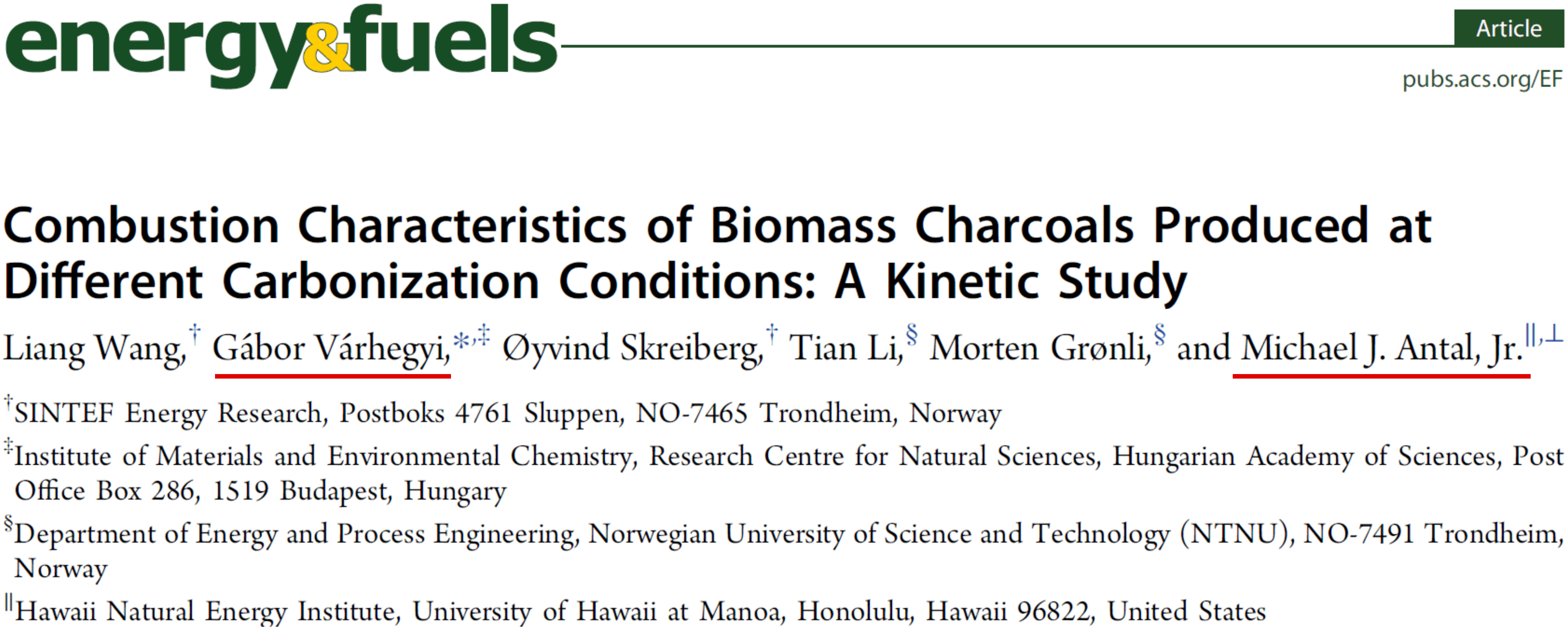
Testing the prediction capabilities of the model: The intensity of ion CH_3^+ (methane) was described by one DAEM reaction. The evaluation of two linear T(t) experiments allowed a prediction at a stepwise T(t).

A simple prediction test, 2002, *continued*



Testing the prediction capabilities of the model: The intensity of ion CH_3^+ (methane) was described by one DAEM reaction. The evaluation of two linear T(t) experiments allowed a prediction at a stepwise T(t).

The last common work, published in April 2016: Both of us participated in the BioCarb+ project of SINTEF, Norway, with Liang Wang, Øyvind Skreiberg, Morten Grønli, *et al.*



energy&fuels

Article

pubs.acs.org/EF

Combustion Characteristics of Biomass Charcoals Produced at Different Carbonization Conditions: A Kinetic Study

Liang Wang,[†] Gábor Várhegyi,[*,‡] Øyvind Skreiberg,[†] Tian Li,[§] Morten Grønli,[§] and Michael J. Antal, Jr.[‖,⊥]

[†]SINTEF Energy Research, Postboks 4761 Sluppen, NO-7465 Trondheim, Norway

[‡]Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Post Office Box 286, 1519 Budapest, Hungary

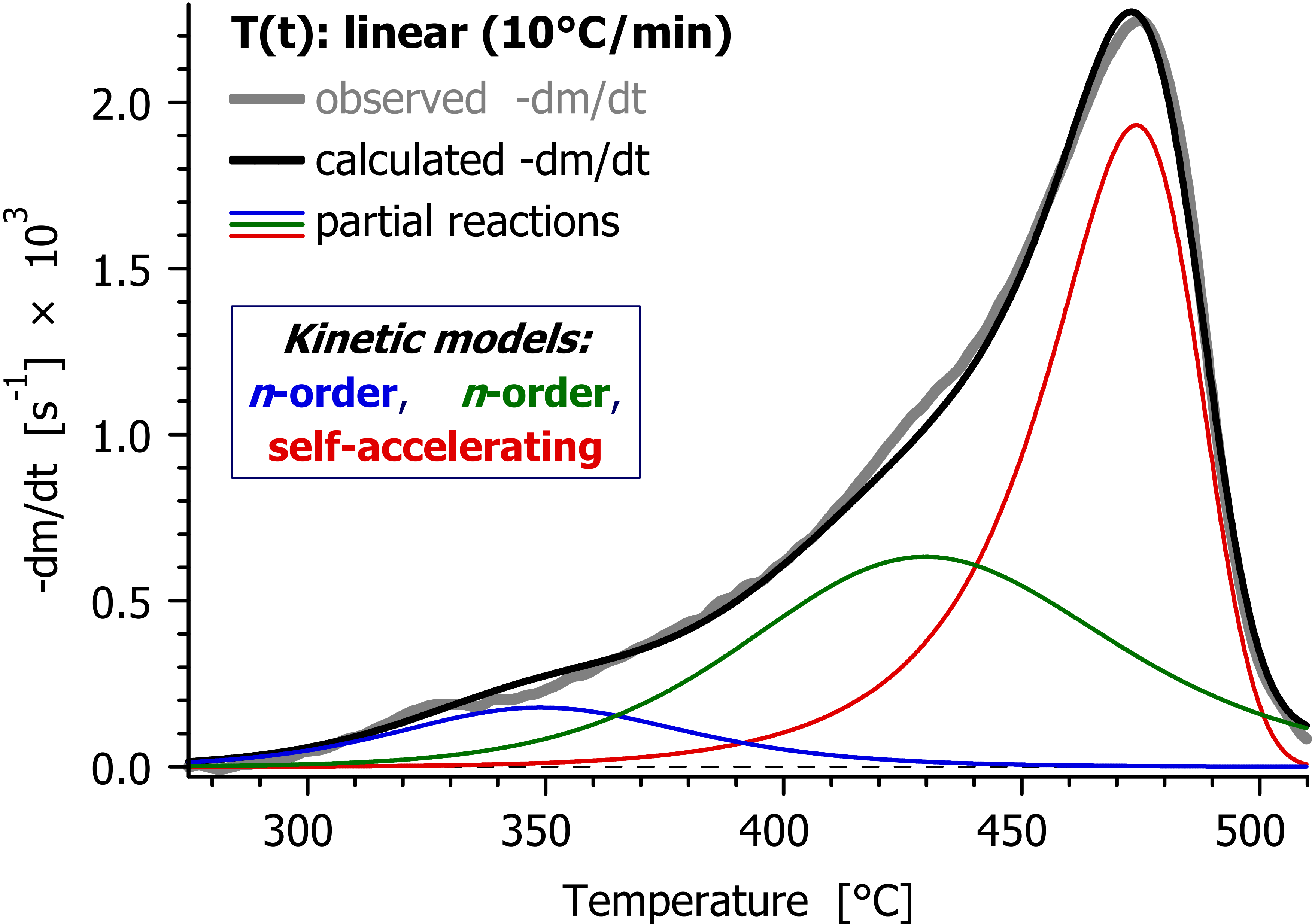
[§]Department of Energy and Process Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway

[‖]Hawaii Natural Energy Institute, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States

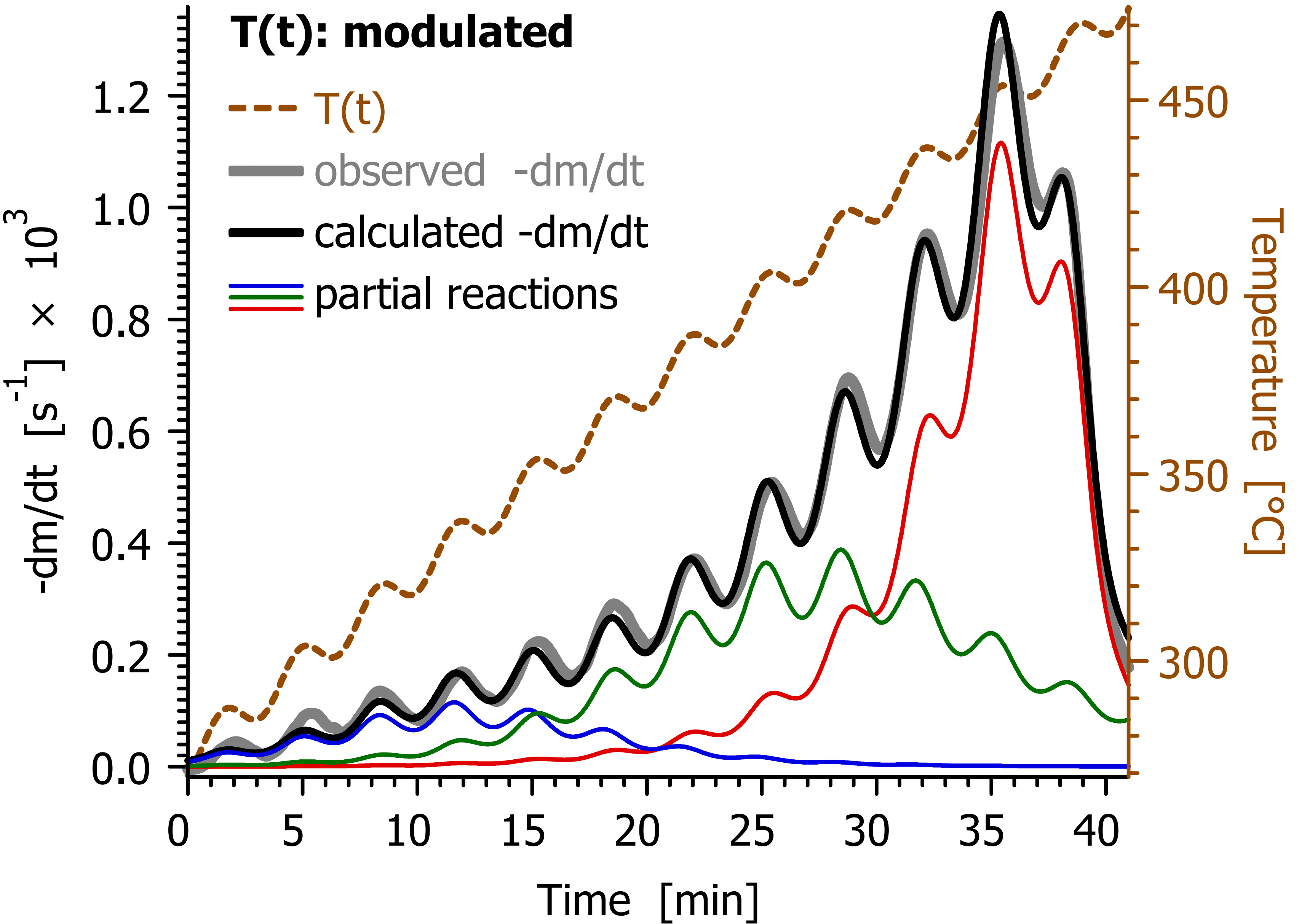
The last common work, published in April 2016:

- Michael's charcoals (produced by his Flash Carbonization™) were compared to chars produced at the same pressure in an open pan, under well-defined conditions. (The atmospheric pressure versions of the latter were also included into the study.)
- Real charcoals contain more and less reactive parts; this property was approximated by the assumptions of three pseudo-components.
- The evaluation was based on more than one experiment that differed in temperature programs.
- The series of experiments were evaluated together by the method of least squares.

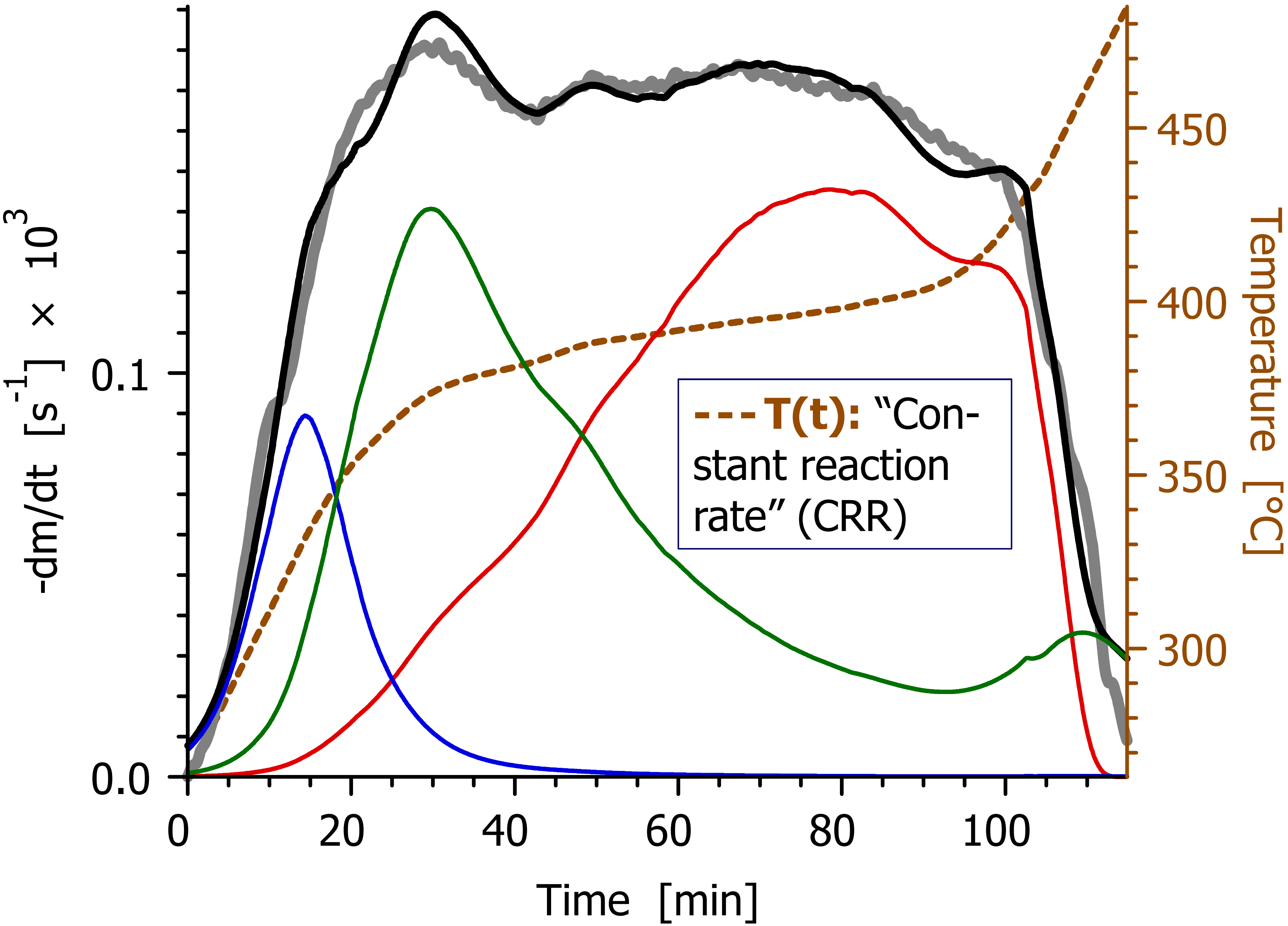
Flash carbonization spruce chars; kinetic evaluation of a series of experiments (published in April, 2016):



Flash carbonization spruce chars; kinetic evaluation of a series of experiments (published in April, 2016):



Flash carbonization spruce chars; kinetic evaluation of a series of experiments (published in April, 2016):



ACKNOWLEDGMENTS:

Participants in the kinetic part of the cooperation*:

Antal, M. J., Jr. (17); Bourke, J. (1); Dai, X. (1); Grønli, M. (2); Jakab, E. (5); Li, T. (1); Mészáros, E. (1); Mok, W. S. L. (3); Skreiberg, Ø. (1); Székely, T. (1); Szabó, P. (9); Till, F. (1); Várhegyi, G. (17); Wang, L. (1); Zelei, B. (1);

Most important funders of this cooperation:

National Science Found (USA); the Coral Industries Endowment in the University of Hawaii; the Hungarian National Research Fund (OTKA), and the US – Hungarian Science and Technology Joint Fund.

*The figures in the parentheses indicate the number of the corresponding publications. Altogether 17 articles belong to the kinetic parts of the work. They were cited ca. 2500 times.

Here is the end of this presentation.

It's not yet the end of the road. But the rest of the work should be continued without Michael.

Thanks for you kind attention.

APPENDIX:

Info and photos about the special soirée where this lecture was presented and a poster about the life of Michael Jerry Antal, Jr.

Part of the flier on this special event:

SPECIAL
SESSION

Soirée in the Fine Arts Museum of Nancy,
9 May 2016, 17:00-21:00
to honour the late Michael J. Antal Jr

« I looked forward to your meeting more than any other in my life »

Michael J. Antal, Jr, a leading biomass researcher, died on 21 October 2015.

He received his MS degree in Applied Physics (Quantum Mechanics and Electromagnetic Theory) from Harvard University followed by a PhD degree in Applied Mathematics (Numerical Analysis and Quantum Mechanics), also from Harvard Universi-

During the planning period of PYRO2016, Michael suggested a special evening linking art, science and history together. However, he was already seriously ill when he received a request for an invited keynote lecture entitled “The art, archaeology, and history of wood pyrolysis” at PYRO2016.

That was when he answered: “I looked forward to your meeting more than any other in my life ”. Indeed he hoped to prepare his lecture but sadly Michael passed away before he could finish it.

His death changed the course of the special evening that was planned to take place in the Museum of Fine Arts. Now the focus is on a commemoration of Michael.

The Museum of Fine Arts, part of a UNESCO World Heritage Site

Prof. Michael Jerry Antal Jr.

"I have looked forward to your meeting more than any other in my life."

Soirée in the Museum of Fine Arts of Nancy,
9 May 2016, within the frame of the 21st
Symposium on Analytical and Applied Pyrolysis
to honor the Late Michael J. Antal, Jr

Michael J. Antal, Jr, a leading person in biomass research, died on 21 October 2015.

He received his MS degree in Applied Physics (Quantum Mechanics and Electromagnetic Theory) from Harvard University, followed by the PhD degree in Applied Mathematics (Numerical Analysis and Quantum Mechanics), also from Harvard University.

In 1973, he started his professional career at Los Alamos National Laboratory as a staff member of the Thermonuclear Weapons Physics Group. However, his research interests soon turned to topics related to the sustainable future of mankind.

In 1976, he published his first pioneering work on the peaceful use of solar energy in the production of fuels from biomass and municipal wastes.

After serving as an assistant professor at Princeton University, he was selected as the recipient of the Coral Industries Endowed Chair at the University of Hawaii in 1982, where he became a full professor and the Coral Industries Distinguished Professor of Renewable Energy Resources.

He achieved outstanding results in practically all areas of biomass research and development, including the pyrolysis of biomass materials, and the formation of charcoals through pyrolytic reactions.

Presently the Scopus database reports more than 10 600 citations for 175 articles published with his authorship. The corresponding *h*-index is 54. A selection of his widely cited works is also shown in this poster.

During the planning period of PYRO2016, Michael suggested a special soirée linking art, science and history together. However, he was already seriously ill when he received a request for an invited keynote lecture entitled *"The art, archaeology, and history of wood pyrolysis"* at PYRO2016. That was when he answered: "I have looked forward to your meeting more than any other in my life." But he hoped to prepare his lecture. Sadly, Michael passed away before he could finish it.

His death changed the course of the special soiree that was planned to take place in the Museum of Fine Arts. Now the focus is on a commemoration of Michael.

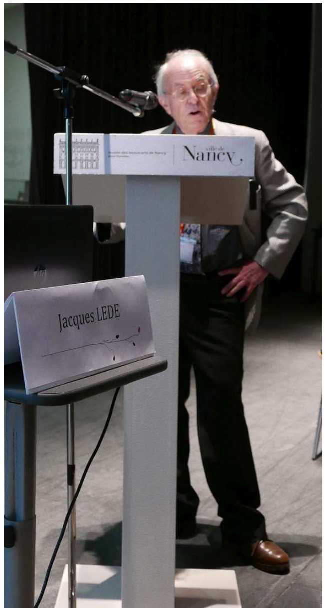
1987 April, Honolulu, in Michael's lab
Front row: Michael with graduate students Tongchit Leesomboon and Ravi Narayan
Back row: Gábor Várhegyi and William Shu-Lai Mok

2006 June, Budapest
Cherry soup with his wife and daughter in the home of Gábor Várhegyi

2012 2012 June, Košice, Slovakia
Photo from a trip: Michael sat down on the grass and read a book on the physics of the universe while the rest of the company visited a less interesting exhibition.

2014 April, Trondheim, Norway, in the laboratory of SINTEF
From left to right: Liang Wang, Øyvind Skreiberg, Gábor Várhegyi and Michael.
Photo by Thor Nielsen. Courtesy by SINTEF, Norway.

Ann Antal



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