Korean J. Chem. Eng., **20**(4), 631-634 (2003)

SHORT COMMUNICATION

Conversion of CH_4 and CO_2 to Syngas and Higher Hydrocarbons Using Dielectric Barrier Discharge

Bae-Bok Hwang, Yeong-Koo Yeo† and Byung-Ki Na*

Dept. of Chemical Engineering, Hanyang University, Seoul 133-791, Korea
*Clean Technology Center, Korea Institute of Science and Technology, Seoul 136-791, Korea
(*Received 15 November 2002 • accepted 17 March 2003*)

Abstract−The conversion of methane to syngas and other hydrocarbons in dielectric barrier discharge plasma under the presence of CO_2 was investigated. Effects of the input voltage on the conversion of methane and CO_2 and the ratio of syngas were analyzed experimentally. The results of numerical simulations showed good quantitative agreement with those of experiments.

Key words: Methane Conversion, Dielectric Barrier Discharge, Syngas, Electron Energy Distribution

INTRODUCTION

CO_2 fixation has attracted much attention due to environmental considerations. There are two major objectives in the recovery and utilization of CO_2: to reduce the greenhouse effects and to use CO_2 as carbon sources to manufacture various chemicals. CO_2 is utilized in the reactions involving C-C, C-H, and C-N bonds and the formation reactions of carboxy and carbonyl compounds [Eliasson and Liu, 2000]. The oxidation of other hydrocarbons using CO_2 as an oxidant is also important. CH_4 is another major source of greenhouse effects. Scientists have paid much attention to the utilization of CH_4 since the 1980s [Yao et al., 2001; Yanh et al., 2001]. Most research interests focus on the syngas (synthesis gas) formation from CH_4 and CO_2 via the following reaction:

$$CH_4+CO_2 \rightarrow 2H_2+2CO$$

The major products are syngas and C2-C3 hydrocarbons. Syngas is the mixture of hydrogen and carbon monoxide and can be produced from the natural gas, coal, petroleum and biomass. Reforming of hydrocarbon fuels and synthesis of methanol, ethylene or hydrogen from CH_4 has been considered of importance because these products can be used as valuable chemicals, automobile fuel, etc. [Xu et al., 1999; Zhang et al., 2001; Matsumoto et al., 2001]. At present, most commercial processes for the conversion of CH_4 to useful products are indirect processes in which CH_4 is first converted to syngas, a mixture of CO and H_2. Syngas is converted to fuels by the Fisher-Tropsch process and to various chemicals, such as methanol and gasoline, via the MTG process [Dry, 2002]. Syngas is also the main source of hydrogen for refinery processes and ammonia synthesis. The principal routes for the conversion of CH_4 to syngas include the steam reforming (H_2/CO>3).

$$CH_4+H_2O=CO+3H_2-229.7 \text{ kJ/mol}$$

This reaction is highly endothermic resulting in relatively expensive and energy intensive generation of syngas. Steam reactors generally run with excessive amounts of steam in order to prevent the deposition of carbon on the catalyst. Disadvantages of the steam reforming can be summarized as follows:

(i) H_2/CO ratio is much higher than that required in FisherTropsch section.
(ii) Lower CH_4 conversion results in due to the maximum operating temperature below 900 °C.
(iii) The high usage rate of water makes it unsuitable in arid regions.

The following partial oxidation of CH_4 by oxygen generates syngas with a H_2/CO ratio close to 2.0, the ideal ratio for Fisher-Tropsch process only at very high temperature.

$$CH_4+0.5O_2=CO+2H_2+38 \text{ kJ/mol}$$

Without catalysts, the reaction occurs only at very high temperature. The fast reaction of CH_4 with oxygen results in the complete oxidation products of H_2O and CO_2, which is not desirable because expensive hydrogen is converted to water. So far, the partial oxidation of methane to syngas has been restricted to laboratory scale [Vosloo, 2001; Rostrup-Nielsen, 2002].

The non-thermal plasma process has been applied in many different fields such as the destruction of harmful compounds in air or synthesis of some chemicals which otherwise require high temperature and pressure. The process can be used in the synthesis of CH_4, ammonia and fuel cell [Eliasson and Liu, 2001]. Recently a direct conversion of CO_2 and CH_4 into heavier hydrocarbons using the catalytic dielectric barrier discharges was reported.

The dielectric barrier discharge (DBD), commonly used to produce a non-equilibrium plasma at atmospheric pressure, is an effective tool for generating energetic electrons. In plasma chemical reactions, the range of the temperature of the electrons is from 10,000 to 100,000 K, while the actual gas temperature remains at near ambient temperature [Eliasson and Liu, 2000; Yao et al., 2001; Matsumoto et al., 2001]. Although experimental studies on DBD have attracted the attention of many researchers [Jeong et al., 2001], plasma chemistry and kinetics of CH_4 conversion are yet to be analyzed. In this study, both theoretical and experimental investigation on the use of DBD to convert CH_4 and CO_2 are performed. Results

†To whom correspondence should be addressed.
E-mail: ykyeo@hanyang.ac.kr

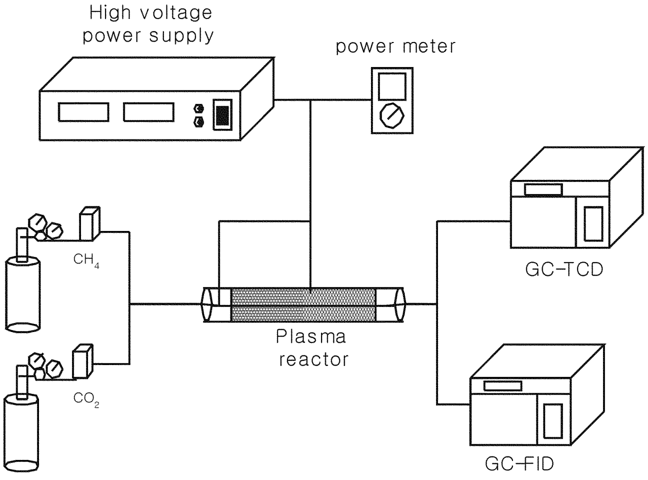

Fig. 1. Schematic diagram of the experimental set up.

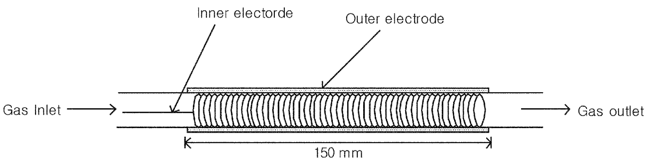

Fig. 2. Construction of the dielectric-barrier discharge reactor.

of computer simulations exhibit the effectiveness of the conversion models proposed in the present study.

EXPERIMENTS

Fig. 1 shows the schematic of the experimental setup. Alumina with inner diameter of 5 mm was used as the dielectric material. The DBD reactor contains a ground metal spring, made of stainless steel. Outer electrode was used with a copper jacket around the reactor wall. Fig. 2 shows the configuration of the DBD reactor. The high voltage generator (Auto electric, Model H1421) is 20 kHz frequency and the voltage and the current are adjustable within ranges of 0-10 kV and 0-100 mA, respectively. The input power is measured by power meter (Metax M3860M). The products are analyzed by two online gas chromatographs (Young-In680D, HP5890) equipped with a PorapakQ,R (1 : 1) and Heysep D which are connected to a TCD (thermal conductivity detector) and an FID (flame ionization detector), respectively. All the experiments were performed at room temperature and atmospheric pressure. The overall conversions and selectivities are defined as follows:

Conversion of CH_4=[(moles of CH_4 in the feed)
−(moles of CH_4 in the products)]
/(moles of CH_4 in the feed)

Conversion of CO_2=[(moles of CO_2 in the feed)
−(moles of CO_2 in the products)]
/(moles of CO_2 in the feed)

Selectivity of CO=(moles of CO produced)/[(moles of CH_4 converted)
+(moles of CO_2 converted)]

Selectivity of H_2=(moles of H_2 produced)/[(moles of CH_4 converted)
+(moles of CO_2 converted)]

Selectivity of C_nH_m=(moles of C_nH_m produced)
/[(moles of CH_4 converted)
+(moles of CO_2 converted)]

MODELING OF THE PLASMA PROCESS

The rate constant of CH_4 dissociation can be given by

$$k_j(T_e)=\int_0^\infty \sqrt{2\varepsilon/m_e}\cdot f(\varepsilon,T_e)\cdot \sigma_j(\varepsilon)d\varepsilon \tag{1}$$

In order for Eq. (1) to be effective, the electron energy distribution function $f(\varepsilon, T_e)$ and the reactive cross section $\sigma_j(\varepsilon)$ should be known. The electron energy distribution function can be obtained from the solution of the Boltzmann equation. In the plasma reaction, measurement of the reaction rate is very difficult because of the electrical energy in the reaction. Use of a molecular velocity distribution function is the usual practice in this case. In the present study the Maxwellian distribution function was adopted in the form parameterized as a function of the electronic temperature:

$$f(\varepsilon,T_e)=0.566\cdot\frac{\sqrt{\varepsilon}}{T_e^{3/2}}\cdot\exp\left(-0.244\cdot\frac{\varepsilon}{T_e}\right) \tag{2}$$

Eq. (2) was found to be adequate to describe the electron energy function in oxygen, CH_4 and silane plasma reaction [Tachibana et al., 1984]. The temperature dependence of the reaction constant can be given by the Arrhenius relation:

$$k(T_e)=AT_e^B\exp(-C/T_e).$$

This relationship can be obtained easily from the combination of Eqs. (1) and (2). But for other species such as C_2H_6, H_2, CO and CO_2, appropriate forms of the Maxwellian electron energy distribution function can be used. For these species it was assumed that k be also represented by the above relation [Yang and Anklam, 2000].

Typical reaction paths are:

$$CH_4\text{-->}CH_3+H \tag{3}$$

$$CO_2\text{-->}CO+O \tag{4}$$

$$CO\text{-->}C+O \tag{5}$$

$$H+H\text{-->}H_2 \tag{6}$$

$$H_2\text{-->}H+H \tag{7}$$

$$CH_3+CH_3\text{-->}C_2H_6 \tag{8}$$

$$C_2H_6\text{-->}CH_3+CH_3 \tag{9}$$

There exist many other reactions. But most of the reaction products obtained in the experiments consist of H_2, CO and C_2H_6 and we can choose reactions (3)-(9) as main reactions to be considered. The rate equations for CH_4, CO_2, H_2, CO and C_2H_6 are given by

$$\frac{dc_{CH_4}}{dt}=q_{CH_4}-k_1\times c_{CH_4} \tag{10}$$

$$\frac{dc_{CO_2}}{dt}=q_{CO_2}-k_2\times c_{CO_2} \tag{11}$$

$$\frac{dc_{H_2}}{dt}=2\times k_4\times c_H-k_5\times c_{H_2} \tag{12}$$

$$\frac{dc_{CO}}{dt}=k_2\times c_{CO_2}-k_3\times c_{CO} \tag{13}$$

$$\frac{dc_{C_2H_6}}{dt}=-2\times k_6\times c_{CH_3}-2\times k_7\times c_{C_2H_6} \quad (14)$$

In Eqs. (10) and (11), q is the molar flow rate of the reactant introduced into the reactor.

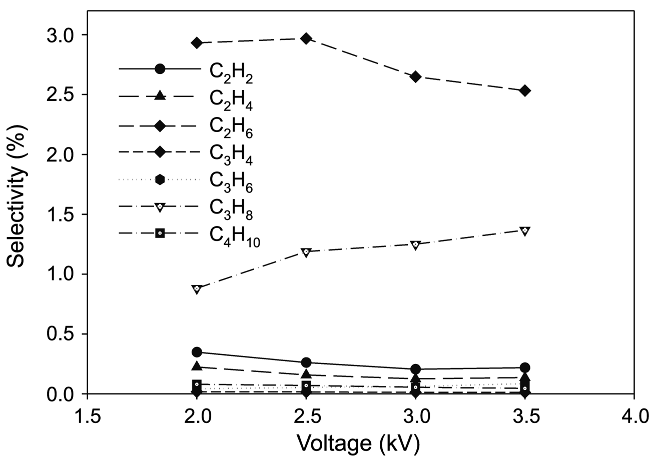

Fig. 3. Influence of the input voltage on CO_2 reforming of CH_4 (Total flow rate=30 sccm; CH_4/CO_2 in the feed=1 : 1; pressure=1 bar).

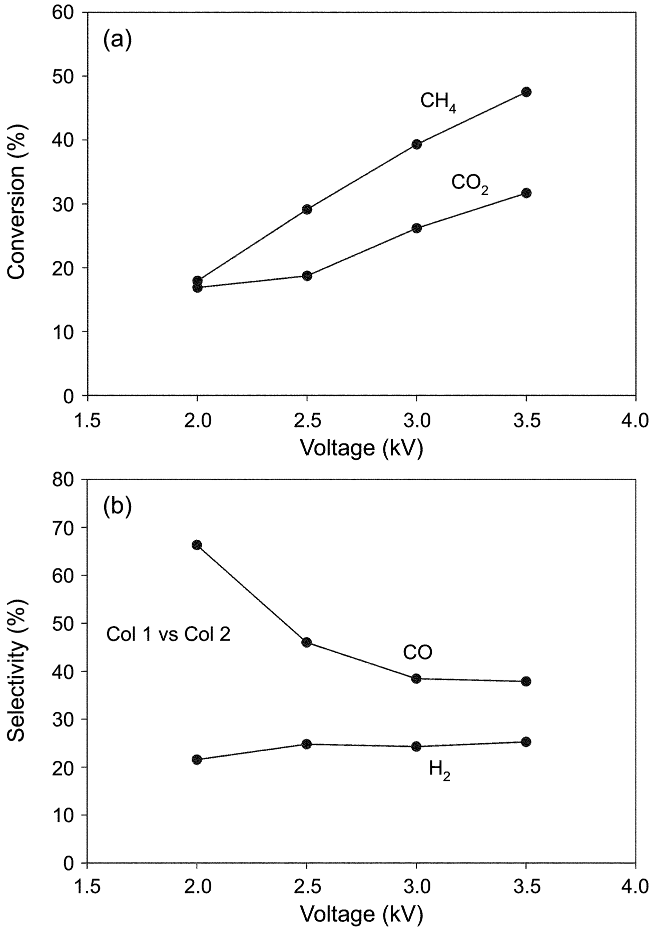

Fig. 4. Influence of input voltage on CO_2 reforming of CH_4: (a) conversion, (b) selectivity (Total flow rate=30 sccm; CH_4/CO_2 in the feed=1 : 1; pressure=1 bar).

RESULTS AND DISCUSSION

The dry reforming of CH_4 with CO_2 is usually carried out at the ratio of 1 : 1 of CH_4 to CO_2, to give a 1 : 1 mixture of H_2 and CO:

$$CH_4+CO_2=2CO+2H_2$$

We first investigated the influence of input voltage on the conversions with initial CH_4 higher than 50%. The relationship between the input voltage and the electron energy can be represented as

$$T_e=p_1-\exp(p_2*V)/p_3$$

In our specific case (at the experimental conditions), p_1=2.0797, p_2=−0.3164 and p_3=0.4875. Conversions of CH_4 and CO_2 increased as the input voltage increased with the conversion of CH_4 higher than that of CO_2. The selectivity of H_2 increased with the increase in input voltage as well, but the selectivity of CO and other products such as C_2H_2, C_2H_4, C_2H_6 and higher hydrocarbons decreased (Fig. 3 and 4). This suggests a mechanism of chain build up from methyl radicals:

$$CH_4+(e, H, O, O^-, OH, \ldots)\rightarrow CH_3+(H, e, H_2, OH, OH^-, \ldots)$$

Thus we can suggest the chain reactions as follows:

$$CH_3+CH_3\rightarrow C_2H_6$$
$$C_2H_6+e\rightarrow C_2H_5+H+e$$
$$C_2H_5+C_2H_5\rightarrow C_4H_{10}$$
$$C_2H_5+CH_3\rightarrow C_3H_8$$

The rate constants (k_1, k_2) of CH_4 and CO_2, measured as a function of input voltage (kV), are shown in Fig. 5 [Tachibana et al., 1984]. As can be seen from the Fig. 5, k_1 and k_2 are nearly proportional to the input voltage (kV).

The dissociation of CH_4 and CO_2 was calculated through kinetic Eqs. (10)-(14) as a function of input voltage. The results as well as experimental data are shown in Fig. 6. From the comparison between experiments and simulations, we can see the effectiveness of the proposed kinetic model. Results of computations on the compositions as a function of the supplied input voltage are illustrated in Fig. 7.

CONCLUSIONS

Effects of the input voltage on methane and CO_2 conversions in

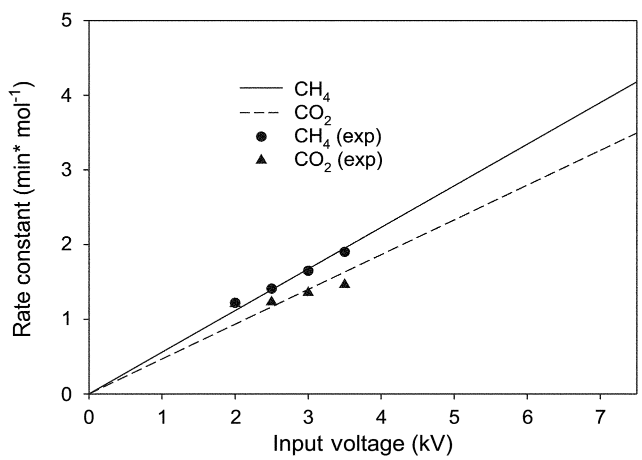

Fig. 5. Rate constant of CH_4, CO_2 as functions of input voltage.

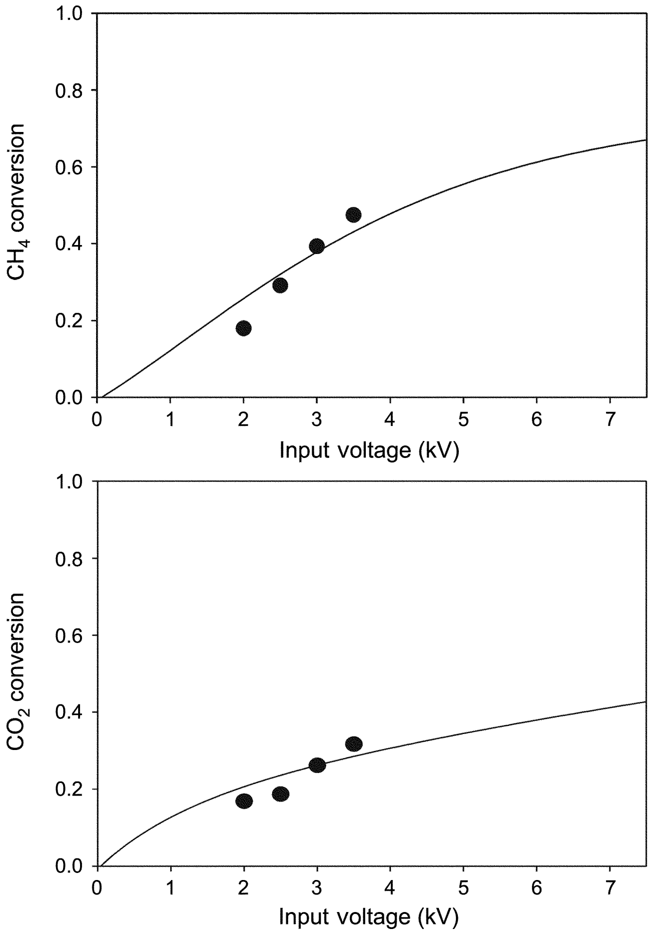

Fig. 6. Dissociation degree of CH_4 and CO_2: - computation, ● experimental (Total flow rate=30 sccm; CH_4/CO_2 in the feed= 1 : 1; pressure=1 bar).

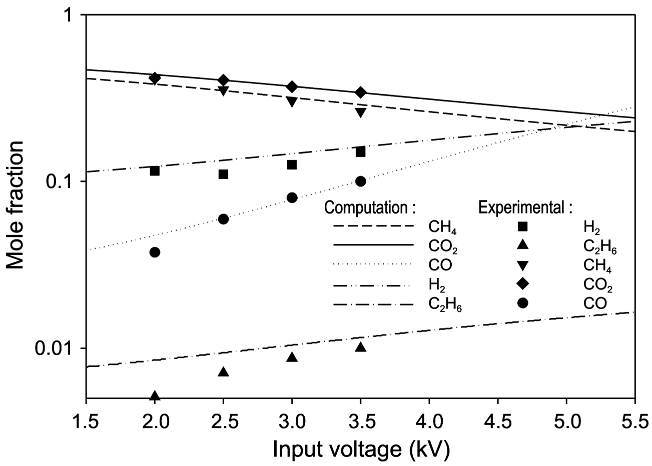

Fig. 7. Effects of the input voltage on the composition.

dielectric barrier discharge were investigated experimentally. As the input voltage increased, conversions and the ratio of syngas increased, while the selectivity of CO, C_2H_2, C_2H_4 and C_2H_6 was decreased. Decreasing selectivity of light hydrocarbons with increase of the input voltage means that increased voltage reduces light hydrocarbons and converts them to other heavier hydrocarbons. Results of numerical simulations showed good agreement with experimental data.

NOMENCLATURE

c_i : molar concentration of species "i" [mol/cm^3]
m_e : mass of the electron [kg]
k_m : rate constant of reaction step "m" [min/cm^3]
T_e : electrons temperature [eV]
ε : electrons kinetic energy [eV]
$\sigma_j(\varepsilon)$: reactive cross section [cm^2]

REFERENCES

Busch, C., "Some Aspect of the Chemical Kinetics of a Reactive Molecular Plasma," *Contrib. Plasma Phys*., **40**, 1 (2000).

Dry, M. E., "The Fisher-Tropsch Process: 1950-2000," *Catalysis Today*, **71**, 227 (2002).

Eliasson, B. and Liu, C.-j., "Dielectric Conversion of Methane and Carbon Dioxide to Higher Hydrocarbons Using Catalytic Dielectric Barrier Discharges with Zeolites," *Ind. Eng. Chem. Res.*, **39**, 1221 (2000).

Eliasson, B. and Liu, C.-j., "Methane Conversion to Higher Hydrocarbons in the Presence of Carbon Dioxide Using Discharge Plasmas," *Plasma Chemistry and Plasma Processing*, **21**, 301 (2001).

Jeong, H.-K., Kim, S.-C., Han, C. and Na, B.-K., "Conversion of Methane to Higher Hydrocarbons in Pulsed DC Barrier Discharge at Atmospheric Pressure," *Korean J. Chem. Eng*., **18**, 196 (2001).

Li, Y., Xu, G.-h., Liu, C.-j., Eliasson, B. and Xue, B.-Z., "Co-generation of Syngas and Higher Hydrocarbons from CO_2 and CH_4 Using Dielectric-Barrier Discharge: Effect of Electrode Materials," *Energy & Fuels*, **15**, 299 (2001).

Masi, M. and Cavallotti, C., "Different Approaches for Methane Plasmas Modeling," *Chem. Eng. Sci.*, **35**, 3875 (1998).

Matsumoto, H., Tanabe, S., Okitsu, K., Hayashi, Y. and Suib, S. L., "Selective Oxidation of Methane to Methanol and Formaldehyde with Nitrous Oxide in a Dielectric-Barrier Discharge-Plasma Reactor," *J. Phys. Chem. A*, **105**, 5304 (2001).

Rostrup-Nielsen, J. R., "Syngas in Perspective," *Catalysis Today*, **71**, 243 (2002).

Tachibana, K., Nishida, M., Harima, H. and Urano, Y., "Diagnostics and Modelling of a Methane Plasma Used in the Chemical Vapour Deposition of Amorphous Carbon Films," *J. Phys. D: Appl. Phys*., **17**, 1727 (1984).

Vosloo, A. C., "Fisher-Tropsch: A Futuristic View," *Fuel Processing Technology*, **71**, 149 (2001).

Xu, H., Shi, K., Yanchen, Zhang, Y., Xu, G. and Wei, Y., "A Study on the Reforming of Natural Gas with Steam, Oxygen and Carbon Dioxide to Produce Syngas for Methanol Feedstock," *Journal of Molecular Catalysis A*, **147**, 41 (1999).

Yang, Y. and Anklam, K., "An Experimental and Modeling Study on the Non-oxidative Methane Conversion in a Dielectric Barrier Discharge," Proc. Hakone VII, Greifswald, **2**, 267 (2000).

Yao, S. L., Okumoto, M., Nakayama, A. and Suzuki, E., "Plasma Reforming and Coupling of Methane with Carbon Dioxide," *Energy & Fuels*, **15**, 1295 (2001).

Zhang, K., Kogelschatz, U. and Eliasson, B., "Conversion of Greenhouse Gases to Synthesis Gas and Higher Hydrocarbons," *Energy & Fuels*, **15**, 395 (2001).