https://doi.org/10.46813/2022-142-084

KINETIC SIMULATON OF CO_2 CONVERSION IN LOW-PRESSURE ELECTRODELESS PLASMA

S. Dudin, V. Lisovskiy, P. Platonov, S. Rezunenko

V.N. Karazin Kharkiv National University, Kharkiv, Ukraine

E-mail: dudin@karazin.ua

Kinetic model of processes in low-pressure inductively coupled plasma describing the carbon dioxide conversion is presented together with the modeling results. The model takes into account only direct electron impact dissociation of carbon dioxide and is valid at the lowest gas pressures and at a reduced electric field > 150 Td. The influence of the gas mixture composition and the plasma density on the electron distribution function has been studied. In the low power limit when *e-e* collisions don't play a significant role the EEDF is strongly non-Maxwellian, but with the plasma density increase, EEDF is approaching Maxwellian distribution. Nitrogen and argon were studied as additions to CO_2. The influence of the calculated distribution function on the energy efficiency of carbon dioxide conversion has been studied. It was concluded that the electron temperature is the key parameter for the energy efficiency, which increases by a factor of 6 with temperature change from 3 to 10 eV and at T_e = 10 eV reaches values of more than 6 %. Comparison of the calculation results with experimental data shows satisfactory agreement.

PACS: 52.77.-j, 82.33.Xj

INTRODUCTION

The development of effective methods for the conversion of carbon dioxide is one of the most urgent scientific problems of recent decades. Various researchers are trying to solve this problem with different methods, and one of the most promising directions is the plasma conversion of carbon dioxide [1-3]. The parameters of non-equilibrium non-thermal plasma are well suited for the conversion [4, 5], and CO_2 conversion into chemical fuels is possible using variable plasma-chemical reactions [6].

Wide variety of gas discharges was tried as the basis for efficient reactor for CO_2 conversion, beginning from lowest pressure up to atmospheric pressure discharges. It was found that at intermediate pressure around 100…300 Torr, sequential excitation of vibrational modes of molecules can increase the energy efficiency for CO_2 dissociation significantly [4]. A necessary condition for this is the low electron temperatures $T_e \approx 1...2$ eV, which are typical for the indicated pressure range.

However, the low-pressure range can also be promising. Previously, we studied the process of CO_2 conversion in a number of low-pressure gas-discharge plasmas: in inductively coupled plasma (ICP) [7], in magnetron and ion-beam plasma [8], and in glow discharge with flat cathode [9, 10].

The key result of [7] is that for ICP, the conversion factor and energy efficiency are relatively high at the lowest pressures (starting from 2 mTorr), decrease with increasing pressure (up to 10 mTorr), and then begin to increase again.

It is well known that ICP is characterized by a direct monotonic relationship between gas pressure and electron temperature [11]. It was concluded in [7] that at the lowest pressures, with relatively high electron temperature $T_e > 3$ eV, the main channel of CO_2 molecule splitting is the direct dissociation by electron impact. The electron temperature decrease with the pressure growth leads to redistribution of energy losses not in favor of dissociation, and the efficiency drops. However, at the temperatures below 3 eV, the cascade mechanism of dissociation through successive excitation of vibrational molecular levels gains strength, and the efficiency increases strongly.

However, the mentioned conclusion was made without theoretical substantiation. In the present study, we have built a kinetic model of processes in low-pressure inductively coupled plasma describing the carbon dioxide conversion. The model is focused on the regularities of direct electron impact carbon dioxide dissociation, which plays a major role at the lowest gas pressures. In [7, 8], the dependences of the conversion coefficient and energy efficiency on pressure are given. In addition, the results of probe measurements of plasma density and electron temperature can be found in [7]. These experimental data allow to compare the simulation results with the real world.

1. MODEL DESCRIPTION

The model considers a cylindrical plasma-chemical reactor with inductively coupled plasma (ICP). In the volume of the reactor, both initial gases and gases formed as a result of the plasma-chemical reaction of carbon dioxide conversion are simultaneously present. The model is zero-dimensional, it assumes that the plasma and gas mixture are homogeneous throughout the entire volume of the reactor.

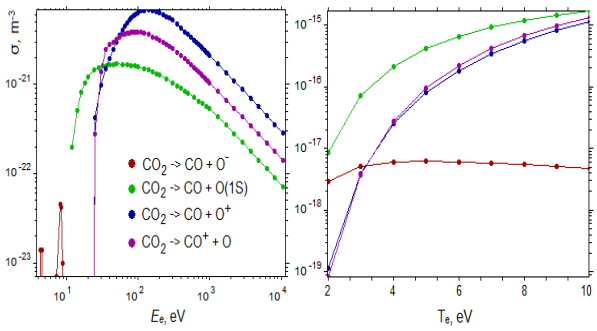
The initial parameters for compiling the gas mixture in the model are the molecular fraction of nitrogen and the conversion factor. The gas mixture was composed according to the following rules:

- the molecular fraction of nitrogen (or argon) ν remains unchanged as a result of the conversion;

- the remaining share (1 - ν) is distributed between carbon dioxide and reaction products in accordance with the given conversion coefficient χ: the share of CO_2 is $(1 – \chi)(1 – \nu)$, the share of CO is $2/3\ \chi(1 – \nu)$, the proportion of O_2 is $1/3\ \chi(1 – \nu)$.

Collision cross-sections for the listed gases were taken from the LXC at resource (https://nl.lxcat.net). The total amount of processes was 76. It should be mentioned that complete reaction kinetics model in CO_2 plasma is quite complicated and includes more than 100 species with more than 10000 reactions [12, 13]. This complexity is raised from the large number of vibrationally excited states of CO_2 molecule that are the steps for its dissociation through the "vibrational ladder" mechanism. However, the main focus of the present research is the direct dissociation by electron impact, which is the main dissociation channel at the lowest gas pressures (the highest values of electron temperature). Thus, the dissociation through sequential excitation of vibrational energy levels is not taken into account in the model, and its applicability is strongly restricted by the condition $T_e > 3$ eV.

Four electron-impact processes are known leading to CO and O creation in different charging states. The cross sections and reaction rates for these processes are shown in Fig. 1. One can see that the dissociative attachment may be neglected for electron temperatures more than 3 eV. The direct dissociation rate is the highest at all the researched electron temperatures while the dissociative ionization cross-sections are higher at electron energies of more than 40 eV.



a b

Fig. 1. Collision cross sections (a) and reaction rates (b) for processes leading to CO_2 molecule splitting into CO and O

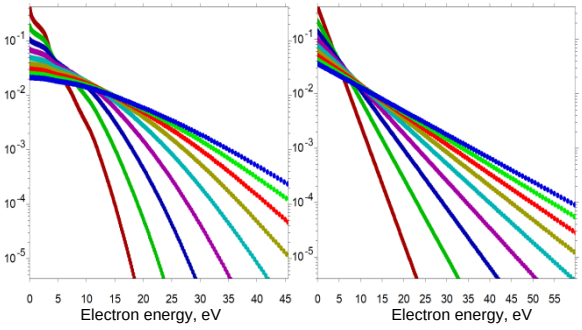
One of the objectives of the present research was to study the influence of the electron energy distribution function (EEDF) on the conversion process, especially on the distribution of electron energy losses in various channels. The BOLSIG + code [14] was used to calculate the EEDF and its effect on the carbon dioxide conversion process.

To calculate the energy efficiency of carbon dioxide conversion, the electron energy losses for the dissociation processes mentioned above were divided by the total energy losses, which included volume losses in all elastic and inelastic collisions and the kinetic energy losses of charged particles escaping to the chamber surface [11]. The energy losses in elastic and inelastic collisions were calculated using the BOLSIG code, and original software was developed to automate the enumeration of its parameters.

2. RESULTS AND DISCUSSION

At the beginning of this section, the influence of the composition of the gas mixture and the plasma density in the reactor on the electron distribution function is considered. Then we study the influence of the calculated distribution function on the energy efficiency of carbon dioxide conversion. At the end, the question of the influence of other gas additions to the initial carbon dioxide on the energy efficiency of the conversion is studied. Finally, the calculation results are compared with the experimental data.

Fig. 2 shows a family of distribution functions with effective temperatures from 2 to 10 eV for two limiting cases of plasma density. Fig. 2,a shows the EEDFs for the case when *e-e* collisions don't play a significant role, that is valid for the limiting case of very low power. It can be seen that the EEDF is strongly non-Maxwellian as a result of the influence of various inelastic processes. The effective electron temperature $T_{e(eff)}$ was determined as 2/3 of the average electron energy. Electron-electron collisions in a dense plasma should Maxwellize the EEDF, and in the limiting case of a very dense plasma, all curves should become straight, as in Fig. 2,b.



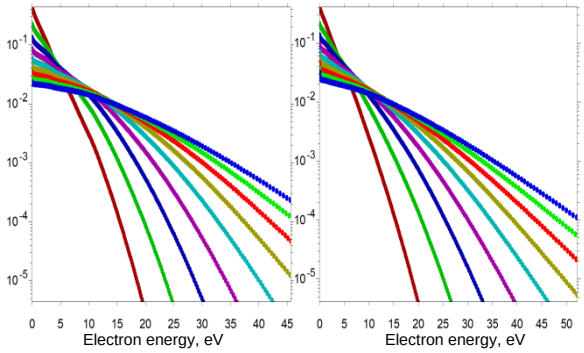
a b

Fig. 2. EEDF evolution depending on plasma density for pure CO_2 (curves for $T_{e(eff)}$ of 2 to 10 eV are collected in each plot): a – no e-e collision (limiting case of very low power); b – Maxwellian distribution (limiting case of very high power)

The EEDF for plasma density of $4 \cdot 10^{16}$ m^{-3} is shown in Fig. 3,a. The Maxwellizing effect of *e-e* collisions is clearly visible, but still we see serious nonlinearities in the EEDF, especially in areas of large cross sections. Fig. 3,b shows a similar EEDF family for a gas mixture typical of partially converted CO_2. As a result of the presence in the plasma volume of a large number of various molecular components with collision cross sections distributed along the energy axis, the EEDF becomes smoother.

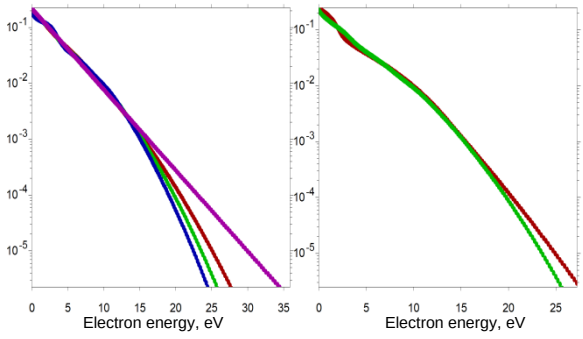
Fig. 4 presents a comparison of different EEDFs for the all cases shown in Figs. 2, 3 as well as comparison of EEDFs for pure CO_2 and for a mixture of 20 % CO_2 and 80 % N_2. One can see that all the curves are nonlinear, excluding the Maxwellian EEDF, which is represented by a straight line. The difference between the EEDFs is not significant excluding the high energy tail. Thus, we

can expect some quantitative effect of the distribution function shape on the CO_2 conversion process, but without significant qualitative change.



a b

Fig. 3. EEDF for ICP with electron density of $4 \cdot 10^{16} m^{-3}$: a – pure CO_2; b – converted CO_2 (conversion factor 60 %)



a b

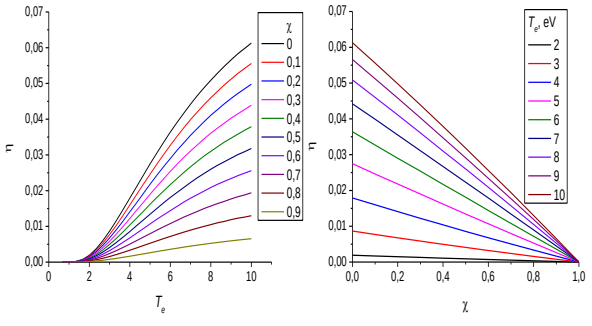
Fig. 4. Comparison of EEDF for $T_{e(eff)} = 3$ eV: a – 4 EEDFs taken from Fig. 2 and Fig. 3; b – EEDFs for pure CO_2 (green line) and for the mixture of 20 % CO_2 and 80 % N_2 (red line)

As mentioned above, the kinetic model makes it possible to calculate the distribution of electron energy losses between different types of collisions. The ratio of the energy loss for the processes responsible for dissociation to the total energy loss allows us to find the energy efficiency of CO_2 conversion.

The calculated dependences of the energy efficiency of conversion η on the electron temperature for the Maxwellian EEDF are shown in Fig. 5,a. One can see that the electron temperature is the key parameter for energy efficiency, which increases by a factor of about 6 with a temperature change from 3 to 10 eV. This can be explained by the fact that the collision cross sections leading to dissociation by direct electron impact become significant only starting from electron energy of 15...20 eV (see Fig. 1).

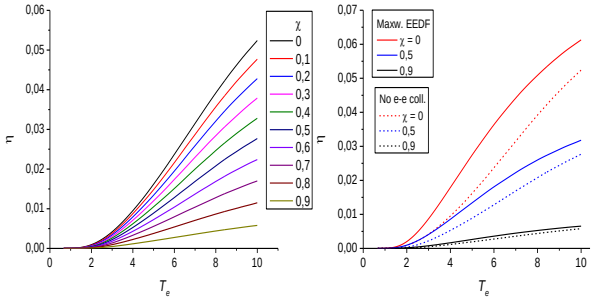
A set of classical dependences of the energy efficiency of conversion η on the coefficient of conversion χ are shown in Fig. 5,b for different electron temperatures. It can be seen that at $T_e = 10$ eV η reaches values of more than 6 % at the minimum conversion coefficients. The energy efficiency decreases monotonically (almost linearly) with increasing χ. This seems natural, given that the higher the conversion rate, the more energy is put into the reaction products rather than into the carbon dioxide.

Let us now consider the influence of the electron distribution function on the energy efficiency of the conversion. Fig. 6 shows the dependences of the energy efficiency of conversion η on the electron temperature for the low-power case when EEDF is non-Maxwellian (see Fig. 2,a) as well as a comparison with the case of Maxwellian EEDF (see Fig. 2,b).



a b

Fig. 5. Calculated dependences of the energy efficiency of conversion η on the electron temperature (a) and on the coefficient of conversion (b) for the Maxwellian EEDF



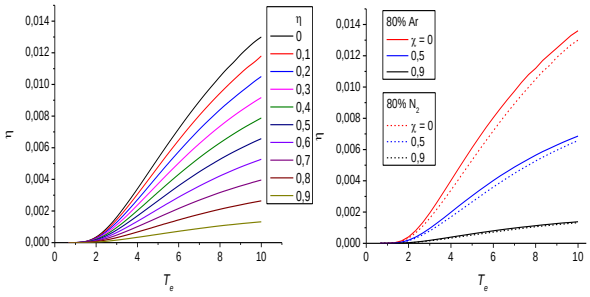
a b

Fig. 6. Calculated dependences of the energy efficiency of conversion η on the electron temperature for the case of no e-e collision (a) and comparison with the Maxwellian case (b)

The typical task for CO_2 conversion with the purpose of environment protection is processing of gas mixtures containing different gases aside from the carbon dioxide. Dedicated calculations were performed to reveal the impact of different gas additions on the carbon dioxide conversion. In all these calculations just Maxwellian EEDF was used. Fig. 7,a depicts the dependences of the energy efficiency of conversion on the electron temperature for the input gas mixture of 20 % CO_2 and 80 % N_2. One can see that the energy efficiency drops by about 5 times in accordance with the CO_2 share in the initial gas mixture while the shape of dependences on electron temperature remains the same. It is interesting to compare the nitrogen impact with other gases.

The argon was chosen for the comparison since it is an atomic gas and its non-elastic collision set does not contain any process for electron energy below 11.5 eV in contrast to molecular gases possessing a number of cross sections of vibrational and rotational excitation being significant at much lower energies.

The comparison between the cases of 80 % N_2 and 80 % Ar is shown in Fig. 7,b. As expected, η is higher for Ar due to the lack of energy loss for molecular levels excitation, but the difference is not substantial.



a b

Fig. 7. Influence of different gas additions on the carbon dioxide conversion: a – dependences of the energy efficiency of conversion η on the electron temperature for the input gas mixture of 20 % CO_2 and 80 % N_2; b – comparison between the cases of 80 % N_2 and 80 % Ar

For the model validation, the comparison of the calculation results with experimental data was performed. The η-χ dependence was calculated for pure CO_2 plasma with non-Maxwellian EEDF, plasma density of $4 \cdot 10^{16}$ m^{-3} and electron temperature of 6 eV. The experimental results for similar conditions were taken from [8]. The comparison of the theoretical and experimental dependences can be found in Fig. 8.

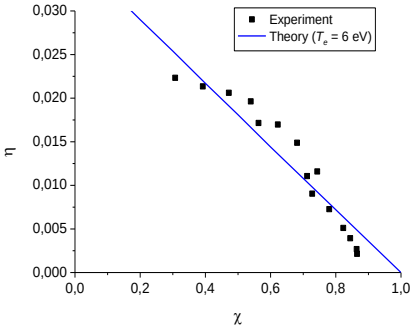


Fig. 8. Comparison of the theoretical and experimental dependences of the energy efficiency of conversion η on the coefficient of conversion χ

One can see reasonable accordance between the theory and the experiment. Experimental data are not available for $\chi < 0.3$ since ICP operation at low RF power was impossible in the system used in the experiments. At the highest χ values, the experimental dependence tends to $\chi \approx 0.87$ while the theoretical curve crosses the horizontal axis exactly at $\chi = 1$. This discrepancy appears because of the model takes into account the CO_2 splitting processes but no reverse process is accounted for. The recombination of CO molecule with atomic or molecular oxygen leading to CO_2 creation may occur both in the plasma volume or on the chamber surface. Three-body volume reactions may be neglected at low pressures while the surface recombination may play a significant role, but the corresponding sticking coefficients are highly dependent on the surface material, and scarce available data are not always in agreement [15].

CONCLUSIONS

Thus, the kinetic model of processes in low-pressure inductively coupled plasma describing the carbon dioxide conversion is described in the present paper together with the modelling results. The model takes into account only direct electron impact dissociation of carbon dioxide neglecting the dissociation through sequential excitation of vibrational levels of CO_2 molecule. Thus, the described model is valid only at the lowest gas pressures, in mTorr range.

The influence of the gas mixture composition and the plasma density in the reactor on the electron distribution function has been studied. In the low power limit when *e-e* collisions don't play a significant role the EEDF is strongly non-Maxwellian as a result of the influence of various inelastic processes. With the input power increase the plasma density is growing, and EEDF is approaching Maxwellian distribution. In order to meet the demands of practical application nitrogen and argon were studied as additions to CO_2. The conclusion was made that EEDF change in response to the gas mixture change is not significant excluding the high energy tail. Thus, one cannot expect a significant effect of the distribution function shape on the CO_2 conversion process.

The influence of the calculated distribution function on the energy efficiency of carbon dioxide conversion has been studied. It was concluded that the electron temperature is the key parameter governing the energy efficiency of the conversion, which increases by a factor of about 6 with the temperature change from 3 to 10 eV. This can be explained by the fact that the collision cross sections leading to dissociation by direct electron impact become significant only starting from electron energy of 15...20 eV.

A set of classical η-χ dependences was calculated for different electron temperatures. At $T_e = 10$ eV η reaches values of more than 6 % at the minimum conversion coefficients and decreases almost linearly with increasing χ. Investigation of the influence of other gas additions to the initial carbon dioxide on the energy efficiency of the conversion has shown that for the case of 80% of nitrogen the energy efficiency drops by about 5 times in accordance with the CO_2 share in the initial gas mixture while the shape of dependences on electron temperature remains the same.

The comparison of the calculation results with experimental data shows satisfactory agreement. Thus, the model may be useful in development of carbon dioxide conversion technologies with use of low-pressure electrode less discharges, like inductive or microwave discharge. Probably, the model may be useful even at atmospheric pressure, for example with Corona or Dielectric Barrier Discharges (DBD), where the vibrational kinetics play a minor role [13]. According to the model, the applicability limit of $T_e = 3$ eV corresponds to the reduced electric field of 150 Td. All the plasmas with stronger electric field fit the approach presented in the present paper. The model validity for description of CO_2 conversion in DBD or Corona plasma is subject of future research.

REFERENCES

1. R. Snoeckx, A. Bogaerts. Plasma technology – a novel solution for CO_2 conversion? // *Chem. Soc. Rev*. 2017, v. 46, p. 5805.
2. A. Bogaerts, G. Centi. Plasma Technology for CO_2 Conversion: A Personal Perspective on Prospects and Gaps // *Frontiers in Energy Research*. 2020, v. 8, p. 111.
3. G. Chen, R. Snyders, N. Britun. CO_2 conversion using catalyst-free and catalyst-assisted plasma-processes: Recent progress and understanding // *Journal of CO_2 Utilization*. 2021, v. 49, p. 101557.
4. A. Fridman. *Plasma chemistry*. Cambridge: "University Press", 2008.
5. J. Amouroux, P. Siffert. Carbon dioxide: a raw material and a future chemical fuel for a sustainable energy industry // *IOP Conference. Series "Materials Science and Engineering"*. 2011, v. 19, p. 012001.
6. C.-j. Liu, G.-h. Xu, T. Wang. Non-thermal plasma approaches in CO2 utilization // *Fuel Processing Technology*. 1999, v. 58, p. 119.
7. S.V. Dudin, A.N. Dakhov. Conversion of carbon dioxide in low-pressure plasma // *Problems of Atomic Science and Technology. Series "Plasma Physics" (118).* 2018, № 6, p. 194.
8. S.V. Dudin, A.V. Zykov, S.D. Yakovin. Plasma assisted conversion of carbon dioxide in low-pressure gas discharges // *Problems of Atomic Science and Technology. Series "Plasma Electrons and New Methods Acceleration" (122).* 2019, № 4, p. 141.
9. V.A. Lisovskiy, S.V. Dudin, P.P. Platonov, V.D. Yegorenkov. Studying CO_2 conversion in dc glow discharge // *Problems of Atomic Science and Technology. Series "Plasma Physics" (130).* 2020, № 6, p. 179.
10. P.P. Platonov, S.V. Dudin, V.A. Lisovskiy. Simulation of gas dynamics in plasma reactor for carbon dioxide conversion // *Problems of Atomic Science and Technology. Series "Plasma Physics" (131).* 2021, № 1, p. 131.
11. M.A. Lieberman, A.J. Lichtenberg. *Principles of Plasma Discharges and Materials Processing*. USA: "John Wiley and Sons", 2005.
12. T. Kozák, A. Bogaerts. Evaluation of the energy efficiency of CO_2 conversion in microwave discharges using a reaction kinetics model // *Plasma Sources Science and Technology*. 2015, v. 24, p. 015024.
13. T. Kozák, A. Bogaerts. Splitting of CO_2 by vibrational excitation in non-equilibrium plasmas: a reaction kinetics model // *Plasma Sources Science and Technology*. 2014, v. 23, p. 045004.
14. G.J.M. Hagelaar, L.C. Pitchford. Solving the Boltzmann equation to obtain electron transport coefficients and rate coefficients for fluid models // *Plasma Sources Science and Technology*. 2005, v. 14, p. 722.
15. A. Vesel, R. Zaplotnik, J. Iacono, M. Balat-Pichelin, M. Mozetic. A Catalytic Sensor for Measurement of Radical Density in CO2 Plasmas // *Sensors*. 2012, v. 12, p. 16168.

Article received 11.10.2022

КІНЕТИЧНЕ МОДЕЛЮВАННЯ КОНВЕРСІЇ CO_2 У БЕЗЕЛЕКТРОДНІЙ ПЛАЗМІ НИЗЬКОГО ТИСКУ

С. Дудін, В. Лісовський, П. Платонов, С. Резуненко

Представлено кінетичну модель процесів у індукційній плазмі низького тиску, що описує конверсію вуглекислого газу, та результати моделювання. Модель враховує лише дисоціацію вуглекислого газу електронним ударом і справедлива за найнижчих тисків газу та при зведеному електричному полі понад 150 Td. Досліджено вплив складу газової суміші та щільності плазми на функцію розподілу електронів. У випадку малої потужності, коли *e*-*e*-зіткнення не відіграють істотну роль, ФРЕЕ є сильно немаксвелівською, але із збільшенням щільності плазми ФРЕЕ наближається до максвелівського розподілу. Азот та аргон вивчалися як добавки до CO_2. Досліджено вплив розрахованої функції розподілу на енергетичну ефективність конверсії вуглекислого газу. Зроблено висновок, що температура електронів є ключовим параметром для енергетичної ефективності, яка збільшується в 6 разів при зміні температури від 3 до 10 еВ та при T_e = 10 еВ досягає значень понад 6 %. Порівняння результатів розрахунку з експериментальними даними показує задовільну згоду.