Comparison of node net-influences on targeted species in bipartite graph-theoretical representaion of plasma chemical reaction networks

T. Holmes[1]

[1] *Department of Chemical and Biological Engineering, The University of Sheffield, Sheffield, UK*

Abstract: A dynamic bipartite variable-relationship graph was used to represent a plasma chemical reaction system. Using this graph, a novel method was used to assess the net-influence of each node on a target node. Species influences were generally found to be much less than the influence of electron energy on the target node. However, examining the effects of individual species would require further investigation comparing the graphical position of species nodes with species net-influence predictions and effects in simulations.

Keywords: Plasma chemistry, graph theory, chemical engineering, optimization, node influence.

1. General

What aspects of a system can be changed in order to optimise it? What effects will such changes have on the rest of the system? Representing changeable aspects of the systems as nodes in a graph is a novel way of approaching this. These nodes can be species, such as ions, radicals, etc., reactions, or with variable-relationship graphs, even variables such as electron energy. These are all aspects of a plasma chemical system that could potentially be altered to improve performance. It has been demonstrated that 0D chemical kinetic models can be represented as bipartite variable-relationship graphs (fig. 1), which can be updated dynamically for time-dependent 0D simulations [1]. In some cases, using these graphs the potential effects of changing node values on a target outcome can be estimated. Recent work has investigated electron energy in this context [1], where it was found that the "net-influence" of electron energy was a predictor of changes to the electron energy sequencing that could increase efficiency or yield of certain target chemicals significantly in 0D plasma chemical simulations. Achieving similar results for species and reactions, however, looks to be a more labyrinthine problem. Presented here is a preliminary further study, comparing the influences of all variable nodes as the first step to a more comprehensive study.

2. Methods – graph, simulation and nodes of influence

A variable-relationship graph of an air plasma chemical reaction set [2] was used, with edges weighted as dynamic functions of the relationship-nodes, as in [1]. Figure 1 gives an example of the variable-relationship graph used.

A 0D plasma chemical reaction sequence was simulated using the air reaction set [2]. As DBD is a common plasma source applied for atmospheric pressure plasma chemistry, electron energy pulses of typical DBD streamer duration [3] were simulated in succession via linear increase and decrease of electron energy to a peak value of 1eV.

The simulation was run with timesteps of 1×10^{-13} seconds to a simulated time of 3.2×10^{-7} seconds. Reaction rates and species concentrations were calculated for each time step and these values were used to update the dynamic VR graph at every 1×10^{-11} second interval, when the graph edge weights were re-evaluated.

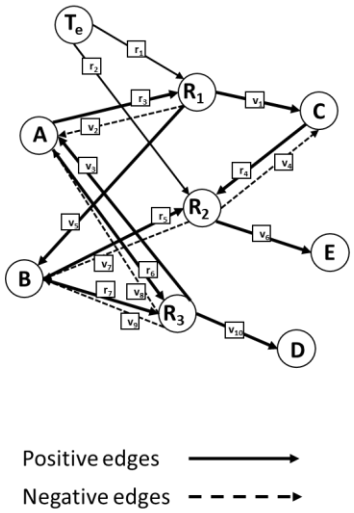

Fig. 1. Diagram of a simple hypothetical VR graph example (copied with permission from [1]) of three reactions (R_1, R_2 and R_3)

The "net-influence" of each node over time on a target node (O_3) was computed using the techniques outlined in [1].

3. Results

The results of this net-influence measure with time of all nodes on a target node (O_3) were plotted as heat maps with logarithmic scale (Fig. 2).

Whilst there was significant variation between species influences, these net-influence values suggest all species variable nodes had significantly less influence than the electron energy and gas temperature variable nodes on the target node. The position of electron energy and gas temperature in the graph could to some extent be used to anticipate this, suggesting prior analysis of graphical positioning of nodes (i.e. relative proximity to other nodes, presence in cycles, in-degree vs out-degree, etc.) presents an opportunity for targeting without the need for simulation, and may warrant further investigation.

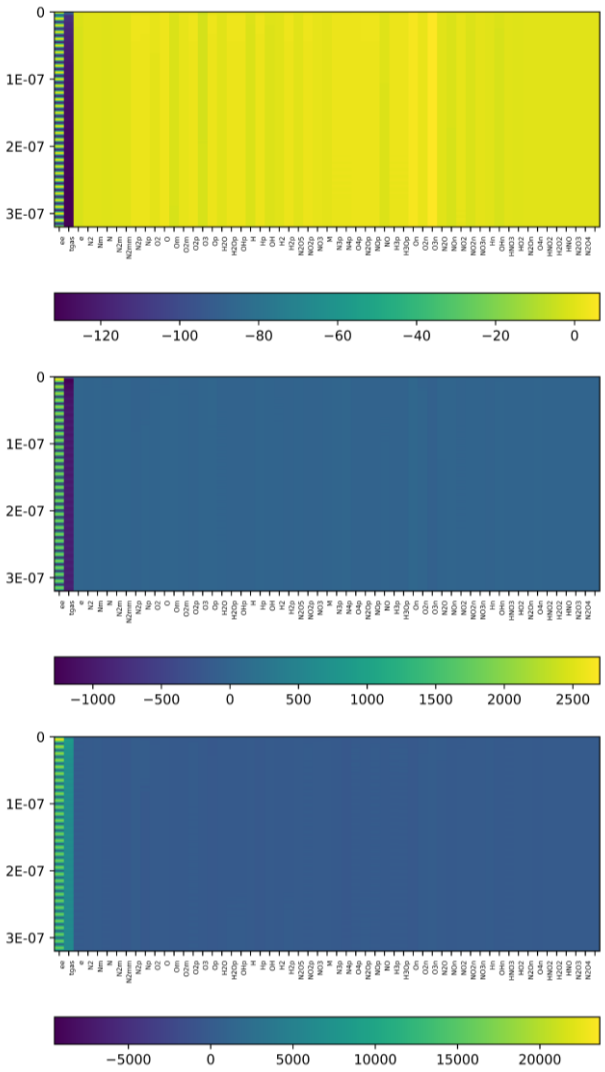

Fig. 2. Heat maps of net-influences of all variable nodes with time for three depths of precursor. Y axis: simulated time in seconds. X axis, species, colour scale bar is arbitrary logarithmic scale for net-influence.

Using the adjacency matrix operations in [1] it was also possible to step back in depths of predecessor from the target node. It was found that some nodes would alternate between positive and negative net-influences in alternate predecessor depths. In the case of electron energy influence [1] these fluctuations through predecessor depths were previously found to be indicative of alternating effects over simulated time when compared with the results of simulations. It is possible that this may also be the case for species influences to a lesser extent, but this will require further investigation, especially as most species are involved in cycles.

However, the efficacy of electron energy [1] suggests the mere presence of cycles is not fundamentally prohibitive to the use of such graphical net-influence measures for optimisation, and even if not all species and reaction nodes may be "targeted" in this way, if the suitability of a node can be evaluated without the need for full simulations (i.e. by merit of its positioning in the graph alone) this would indeed be advantageous, as targeted altering of any species concentrations and reaction rates clearly gives a greater range of options for optimisation of systems involving plasma chemistry.

4. Conclusions

The net-influence of electron energy has previously shown efficacy in the prediction of improved electron energy sequencing for a target output [1]. Comparing all variable-nodes in the system, however, showed the influence of species-nodes to be significantly lower than electron energy and gas temperature on a target node. This suggests that the efficacy of altering species-variables according to the net-influence measures may not be comparable to that for electron energy. Nevertheless, this should be further examined with comparisons of variable-node graph position, variable-node influences, and the effects of altering a variable in simulations, as altering species concentrations according to some influence measure would increase the range of options for this type of optimisation.

5. References

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