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Representing interconversions among volatile fatty acids in the Molly cow model

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ABSTRACT

The Molly cow model uses fixed stoichiometric coefficients for predicting volatile fatty acid (VFA) production from the fermented individual dietary nutrient fractions of forage and concentrate. We previously showed that predictions of VFA production had large errors and hypothesized that it was due to a lack of representation of carbon exchange among VFA. The objectives of the present study were to add VFA interconversion equations based on thermodynamics to the Molly cow model and evaluate the effect of these additions on model accuracy and precision of VFA predictions. Previously described thermodynamic equations were introduced to represent interconversions among VFA. The model was further modified to predict de novo acetate, propionate, and butyrate production coefficients based on forage-to-concentrate ratios rather than discrete, fixed sets of coefficients for forage-based, concentrate-based, and mixed diets. Both the original model and the modified one were reparameterized and evaluated against a common data set containing 8 studies reporting pH, VFA concentration, and VFA production rates using isotope dilution techniques and 62 studies reporting VFA concentrations and pH. Evaluations after parameter estimation revealed that predictions of VFA production rates were not improved, with root mean squared prediction errors (RMSPE) of 77, 60, and 51% for acetate, propionate, and butyrate, respectively, for the revised model versus 75, 63, and 55, respectively, for the original model. The RMSPE for predictions of VFA concentrations were reduced from 28, 46, and 40% to 22, 31, and 26% for acetate, propionate, and butyrate, respectively, simply by rederiving the VFA coefficients, but minimal further improvement was achieved with the addition of thermodynamically driven interconversion equations (RMSPE of 21, 32, and 27% for acetate, propionate, and butyrate, respectively). Thus, the results indicate that thermodynamically driven interchanges among VFA, as represented in this study, may not be a primary determinant for the accuracy of predictions of net production rates. Including the effect of pH on VFA absorption reduced the mean bias of propionate production and slope bias of acetate production, but not the overall RMSPE. The larger prediction errors for VFA production as compared with concentrations suggest the data quality may not be high, or that our representation of VFA production and absorption as well as ruminal digestion is inadequate. Additional data are required to discriminate among these hypotheses.
Key words: volatile fatty acids, Molly, isotope dilution

INTRODUCTION

Accurate predictions of VFA production in the rumen are important in representing ruminal function, ruminal efficiency, and environmental impact of ruminants. The Molly cow model (Baldwin, 1995) is a dynamic, mechanistic model that represents nutrient digestion, metabolism, and production of a cow. The VFA predictions therein are based on stoichiometric coefficients described by Murphy et al. (1982) and Argyle and Baldwin (1988). The coefficients represent the fractional mass conversions of fermented substrate to each VFA, and were derived for each of 5 nutrient classes, starch, soluble carbohydrate, cellulose, hemicellulose, and protein, for each of 2 diet types, high-forage and high-concentrate feeding programs. These coefficients are based on the assumptions that the substrate supply is a primary determinant of VFA production rates and VFA interconversions either do not exist or are proportionally constant across diet types. However, our recent study demonstrated that predictions of the VFA production rates, with the use of these coefficients, are associated with large errors (Ghimire et al., 2014).

Dietary changes not only modify the available substrates, but also elements of the ruminal environ-

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ment including pH, hydrogen partial pressure, and VFA concentrations, which will affect thermodynamic states and, thus, the metabolic pathways used by the microbes. Kohn and Boston (2000) estimated that the change in free energy ($\mathbf{\Delta G}$) when glucose is converted to acetate, propionate, and butyrate was −140.2, −144.3, and −178.9, respectively. Such large changes in free energy indicate that glucose production from VFA is unlikely without significant energy consumption, and thus reactions can be expected to proceed in the forward direction rather than the reverse. However, similar ΔG for these reactions also indicates that ΔG of VFA interconversion is close to zero at a fixed ruminal environment, and the rate of interconversion should be governed by thermodynamic changes in the rumen (Ungerfeld and Kohn, 2006). For example, Ungerfeld and Kohn (2006) calculated that acetate to propionate and acetate to butyrate interconversions were −11.2 and 4.2 kJ/mol, respectively, for a high-roughage diet and −12.5 and −2.8 kJ/mol for a high-concentrate diet, with some assumptions on unmeasured reactant and product concentrations. Such small changes in free energy make these reactions more susceptible to changes in dietary composition, which affects the ruminal environment, and changes in VFA interconversion have been reported by Sutton et al. (2003) for those dietary changes.

Thus, the stoichiometric coefficients may not capture the potential variation in net production rates caused by variable interconversions among VFA. Furthermore, the lack of a representation of the effect of pH on VFA absorption in the model may cause inaccurate estimation of VFA concentrations and can affect production rate predictions (Dijkstra et al., 1993; Bannink et al., 1997).

We hypothesized that representing carbon exchange among VFA can improve predictions of VFA production by the Molly cow model. The objective of our study was to introduce thermodynamically driven VFA interconversion equations into the Molly cow model, refit the coefficients describing VFA synthesis and absorption to a literature data set, and evaluate the effect of the changes on prediction errors of VFA production rates and concentrations.

MATERIALS AND METHODS

Model Description

The Molly cow model described by Baldwin (1995) with modifications (Hanigan et al., 2006, 2009, 2013) was used as a starting point (**M13 model**). Simulations were conducted using the acslX software package (V3.0, Aegis Technologies Group Inc., Huntsville, AL). Model simulations of each scenario were run for 10 d of model time to ensure steady state had been achieved, and model results from the last day of the run were compared with observed values.

Murphy et al. (1982) devised VFA stoichiometric coefficients based on the Koong et al. (1975) model and defined the coefficients separately for forage and concentrate based diets using VFA concentration data. Argyle and Baldwin (1988) later added coefficients for a mixed diet set, which was the average of forage and concentrate coefficient sets (Baldwin, 1995). Thus, in the M13 model 1 of the 3 sets of coefficients was used for each diet depending on its forage content (% of dietary DM): forage set when more than 80%, concentrate set when less than 20% and mixed set for the remainder. However, using discrete sets of coefficients introduces discontinuities, which generally are not well tolerated in optimization problems (Floudas and Pardalos, 2008). Therefore, the M13 model was modified to represent de novo VFA stoichiometric coefficients for the mixed diet as a linear interpolation of the concentrate and forage sets using fractional proportion of forage in the diet (f_{For}; 0 to 1) to weight the forage and concentrate coefficients:

$$f_{i,j} = f_{i,j,For} \times f_{For} + f_{i,j,Con} \times (1 - f_{For}), \qquad [1]$$

where $f_{i,j}$ represents the stoichiometric coefficient defining production of each VFA (j = acetate, propionate, or butyrate, mol/mol of hexose equivalent) from each dietary substrate i (i = cellulose, hemicellulose, starch, and soluble carbohydrate). The *For* and *Con* coefficient sets were defined as those derived from diets with 100% forage and 100% concentrate (% of dietary DM), respectively. Based on this abbreviation scheme, for example, *fScPrFor* denotes the coefficient for production of propionate (mol/mol hexose equivalent) from the fermentation of soluble carbohydrate in the forage portion of the diet. The difference in this approach is that, for each diet, both forage and concentrate parameters of each substrate are used to yield a new parameter based on fraction of forage in that diet, whereas in (Baldwin, 1995) discrete sets are used for a diet depending on whether the diet is categorized as forage-based, concentrate-based, or a mixed diet. The model updated with Eq. 1 was denoted as the **M16 model**.

The following equations, described by Ungerfeld and Kohn (2006), were introduced into the M16 model to represent carbon interchange among the VFA (**M16VFA model**):

$$F_{A,P} = K_{A,P}[A][CO_2]P_{H_2}^3\left([ADP][P_i]\left[H^+\right]\right)^n; \qquad [2]$$