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Task 3.9 - Catalytic Tar Cracking

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DISCLAIMER

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1.0 INTRODUCTION

Tar produced in the gasification of coal is deleterious to the operation of downstream equipment including fuel cells, gas turbines, hot-gas stream cleanup filters, and pressure swing adsorption systems. Catalytic cracking of tars to smaller hydrocarbons can be an effective means to remove these tars from gas streams and, in the process, generate useful products, e.g., methane gas, which is crucial to the operation of molten carbonate fuel cells.

The need for on-line cracking of gasification tars is common to many types of gas stream cleanup. Aerosol tars are not readily removed from gas streams by conventional means and often end up plugging filters or fouling fuel cells, turbines, or sorbents. Catalytic cracking of these tars to molecular moieties of C_{10} or smaller would prevent the problems commonly attributed to the tars. As an example, the moving Bourdon (fixed-bed) gasifier by virtue of its efficient countercurrent heat exchange and widespread commercial use may offer the lowest-cost integrated gasification combined cycle (IGCC) system if tar generation and wastewater contamination can be minimized. A project has been undertaken by the Energy & Environmental Research Center (EERC) on catalytic tar cracking to evaluate the potential of selected catalysts to minimize tar accumulation and maximize char conversion to useful liquid and/or gaseous products.

2.0 OBJECTIVES

The objectives of this project arise from two fundamental questions concerning catalytic cracking of tar:

- Can gasification tar be cracked by synthetic nickel-substituted synthetic micamontmorillonite (NiSMM), zeolite, or dolomite material to a product slate that does not contaminate downstream equipment such as ceramic or candle filters, fuel cells, or turbines?

- Can gasification tars be cracked selectively by the catalysts mentioned above to produce a desired liquid and/or gas stream?

3.0 ACCOMPLISHMENTS

3.1 Papers and Publications

The following papers containing the results obtained from the work performed during this project were prepared and presented:

Timpe, R.C.; Kulas, R.W.; Hauserman, W.B.; Sharma, R.; Olson, E.S.; Willson, W.G. "Catalytic Gasification of Coal for the Production of Fuel Cell Feedstock," *In* Proceedings of

the 10th World Hydrogen Energy Conference; Block, D.L.; Veziroglu, T.N., Eds.; **1994**, Vol. 2, pp 843-852.

Timpe, R.C.; Kulas, R.W.; and Young, B.C.; "A Comparison of Zeolite and Dolomite as Gasification Tar Cracking Catalysts," Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem., **1995**, *40* (4), 783-787.

3.2 Final Report

The data have been reduced for presentation in tabular and figure form. The final report will be completed during August 1995.

4.0 FUTURE WORK

This project will end August 31, 1995. The use of dolomite, a naturally occurring mineral, showed great promise as a catalyst for catalytic tar cracking. Additional tests of catalytic cracking of gasification tars with natural minerals such as trona and nahcolite are recommended.

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A software system for the analysis of the "giornate" sequences in frescoes

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organized by the Wall Paintings Section of the United Kingdom Institute for Conservation

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ABSTRACT

This paper reports on a software system for the analysis of the *giornate* sequences in frescoes, based on mathematical modelling. This model takes into account whole *giornate* and the relations defined on them by the temporal precedence in their realisation. A sample application is provided on frescoes by Luca Signorelli in the Cappella di San Brizio in the Orvieto Cathedral.

[Computer software, computer art, fresco, plasters, wall painting, Signorelli]

RIASSUNTO

Viene presentato lo sviluppo di un sistema software per l'analisi della sequenza di esecuzione delle giornate di un affresco. Tale sistema si basa su una modellizzazione matematica che considera da un lato l'insieme delle giornate e dall'altro la particolare relazione tra di esse, definita dalla precedenza temporale nella realizzazione. Viene inoltre fornita un'applicazione del sistema su affreschi eseguiti da Luca Signorelli nella Cappella di San Brizio nel Duomo di Orvieto.

1. PROBLEM DEFINITION

The technique of the fresco needs the execution of the painting directly on the wet plaster, before the carbonatation on its surface; for this reason the plaster must be drawn up only in the zone to be painted in one day (*giornata*). The careful examination of the joint between two adjacent *giornate* allows one to detect the overlapping of the plasters, so it is possible to establish the temporal precedence in the realisation of the interested *giornate*. The examination of the binary relationships concerning all the couples of adjacent *giornate* on the whole surface of a fresco permits to focalize the going on of the works during the execution of the painting. In the case of frescoes having a wide extension, the *giornate* number can be very high, so it is very difficult to consider and to elaborate the whole information concerning the joints.
The software system implemented for the analysis of the *giornate* in fresco paintings is based on a mathematical modelling that takes into account the whole *giornate* and the relation defined on them by the temporal precedence in their realisation. The mathematical model that fits this specific situation is the model of the direct acyclic graphs (dag).

2. CHARACTERISTICS OF THE SYSTEM

In addiction to the temporal sequence the system allows:

- to point out possible anomalies, due to errors in the detection of the direction of the joints among the *giornate*, for example by the indication of the presence of *loops*;
- to simulate and to elaborate the different possible interpretations in the case it is impossible to detect the direction of the joints;
- to improve the readability of the whole *giornate* sequence by clustering selected sub-sequences.

The software system processes information concerning the overlapping of the plaster among one *giornata* and all the other adjacent *giornate*; it automatically eliminates redundant information by applying the *maximal path* algorithm; so it is possible to obtain the correct temporal sequence for the execution of the *giornate*.
The system runs on personal computer under MS-DOS operative system and it does not need any sophisticated configuration. In order to enable the graphic visualisation mode, it is necessary a WINDOWS 3.1 version or greater.
The system makes available to the user a wide number of features, implemented by means of several program modules. The system's features are:

- inserting, updating, deleting and accessing data concerning the plasters overlapping for the whole *giornate* in the fresco;
- detecting possible loops in the graph corresponding to the inserted data;
- processing the graph corresponding to the inserted data yielding an acyclic graph with no redundant information;
- visualising the resulting graph;
- constructing clustered graphs.

The data input occurs after a preliminary numbering of all the *giornate* of the fresco. At this point all that is needed is to enter the couples of numbers corresponding to the adjacent *giornate* and to the direction of their junction.
The inserted graph elaboration is made by a module that implements the *maximal path* algorithm. This elaboration must be preceded by the verification of the loops presence in the graph supplied by the user. This test is automatically carried out by the system which, whenever a loop is detected, points out all the nodes interested by the loop.
The result of the execution of the module based on the *maximal path* algorithm is provided in two distinct modes, depending on the user's choice:

(1) couples of numbers, corresponding to the *giornate*;

(2) the usual graphical representation: nodes connected by arcs.

Before producing clustered graphs a preliminary selection of the graph nodes to be clustered in only one node must be done.

3. LOOPS, LACK OF INFORMATION AND CLUSTERING

A loop occurs when, following the information concerning the joints of two or more *giornate*, the program comes to a previously examined *giornata*; this is a collapse situation because the sequence for the ordered *giornate* assumes a ring structure. The existence of a loop is unacceptable because it is incompatible with the precedence relations inferred by the overlapping of the plasters at the joints. Further, a loop makes the program removing the redundant information non-terminating. In order to avoid such a critical situation, when a loop is detected the program points out this situation and all the *giornate* interested by the loop. This signal allows the user to visualise the loop on the plotting, so it will possible to verify directly on the fresco surface the overlapping of the interested joints and to change the incorrect information in the input file.
If it is not possible to look over the fresco surface, the loop elimination can be done inverting the direction of one or more joints following opportune considerations. Alternatively, it can be done considering as only one *giornata* all the *giornate* that are interested by the loop (in this case the *giornate* must be adjacent).

The absence of information concerning either the recognition of *giornate* or the direction of the plaster overlapping in the joints, can substantially modify the final result; the amount of the produced alteration depends on the information lack in the input data.
In the second case, that is when it is impossible to ascertain the precedence between two adjacent *giornate*, it must be underlined that this circumstance can not be determinant for the reconstruction of the real sequence: in fact the impossibility to establish a precedence relation between two adjacent giornate sometimes can not determine a real loss of information. The system is able to establish if the unregistered information is redundant, i.e. it does not determine any change in the correct ordering, on the other hand it is essential, because its non-registration causes a different solution by the algorithm.
The reconstruction of only one linear sequence is an extremely rare case; in fact, the increment of the number of the *giornate* makes the graph very branched.
Especially for frescoes having a wide extension some considerations concerning the organisation of the work allow one to pick up additional information for the general ordering of all the *giornate*, independently from the study of the joints. For instance it is evident that if it is possible to know the borders due to the level of the scaffold used for the realisation of the

fresco, like it happens between two adjacent *giornate*, it is possible establish a precedence relation between all the *giornate* under the above scaffold level and those under it. This operation allows for clustering the *giornate,* so that during the execution of the program all those *giornate* are treated as one only *giornata*.

4. A SAMPLE APPLICATION

This software system has been tested on the frescoes by Beato Angelico and Luca Signorelli in the Cappella di San Brizio in the Orvieto Cathedral; the whole fresco surface consists of more than 900 *giornate*. In figure 2 is shown the sequence concerning the *giornate* map for the *Hell* painted by Luca Signorelli; the same is shown as a graph in figure 3. In figure 4 and in figure 5 the situation concerning the *Heaven*, in the same Chapel, is shown. In both the maps the supposed levels for the scaffold are shown, they are different for number and tallness in this two scenes; finally in the graphs the *giornate* concerning local correction are shown with round areas.
The comparison of the situation for these two scenes clearly shows that for the *Heaven* the works have been processed in a more articulate way. For the *Hell*, on the contrary, with the exclusion of the branches due to the *giornate* concerning local corrections, four long linear sequences have been evidenced. Stylistic and technical considerations allow one to make the hypothesis that the *Hell* was the first scene frescoed by the painter on the walls of the Chapel, so it is interesting to have verified that this scene is different from the other also for the *giornate* organisation. The less branched structure of the *Hell* could be due to the absence of assistants in the first phase of the works; this circumstance allows to the painter to directly evaluate the problems due to the planning and the realisation of so large scenes. During the recent restore of the whole frescoes in the Chapel it has been verified in the *Hell* a greater number of corrections and *a secco* finishings; these corrections also concern the architectural structure of the scene.

5. BIBLIOGRAPHY

M. Bottoni, M. Cordaro, M.C. Gaetani, B. Provinciali: *Sviluppo di un sistema sperimentale per l'analisi dinamica delle fasi di esecuzione di affreschi. Finalità e fasi del progetto.* 2ª Conferenza Internazionale sulle prove non distruttive, metodi microanalitici e indagini ambientali per lo studio e la conservazione delle opere d'arte, Perugia 17-20 aprile 1988, vol. I 13.1-15.

G. Ausiello, A. Marchetti Spaccamela, M. Protasi*: Teoria e progetto di algoritmi fondamentali*, Franco Angeli, Milano, 1988.

C. Batini, L. Carlucci Aiello, M. Lenzerini, A. Marchetti Spaccamela, A. Miola: *Fondamenti di programmazione dei calcolatori elettronici*, Franco Angeli, Milano, 1992.

Figures

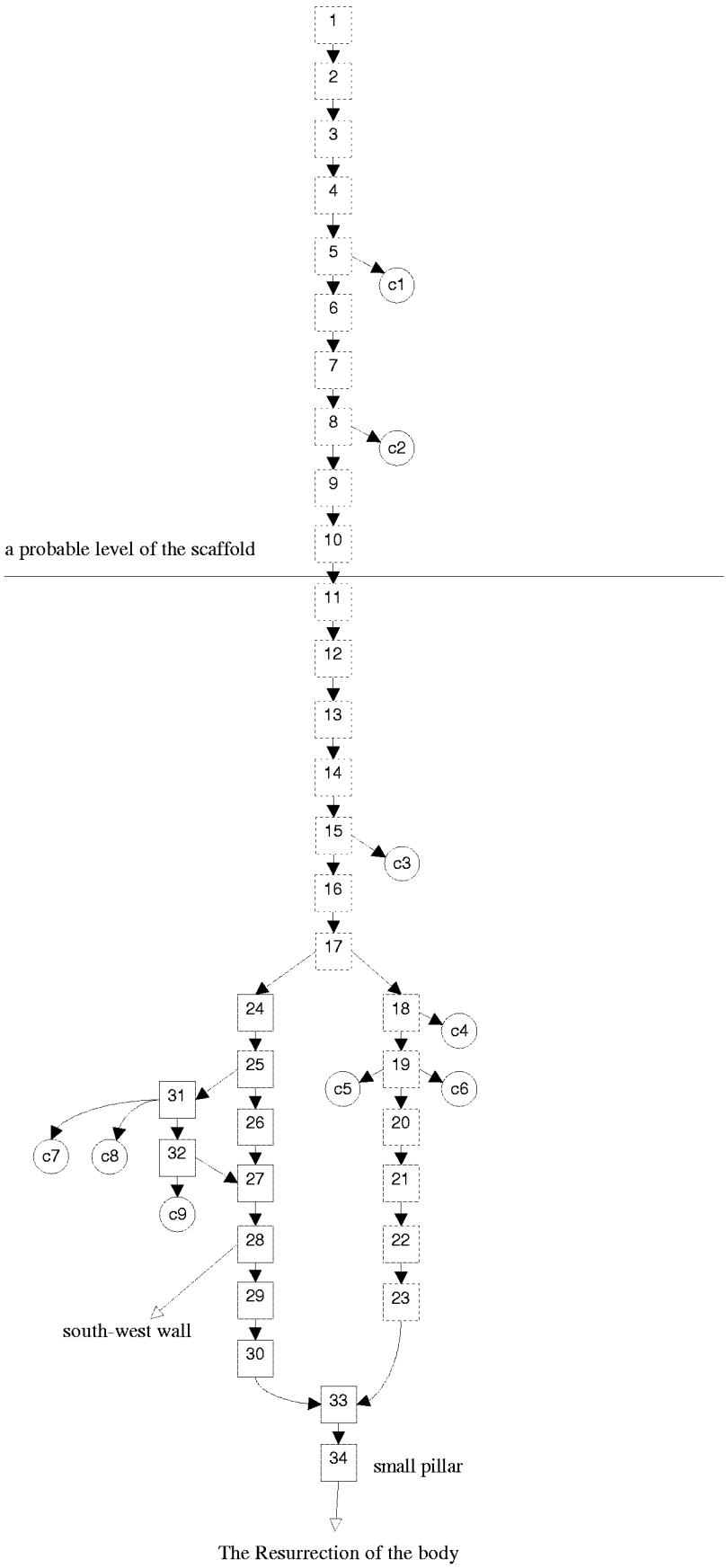
Fig. 1 - Luca Signorelli: the *Hell*. Particular with the overlapping of the plasters at the joint among the *giornate*.

Fig. 2 - Luca Signorelli: the *Hell*. Map of the *giornate* with the paths of the execution sequence.

Fig. 3 - Luca Signorelli: the *Hell*. Sequence of the *giornate*.

Fig. 4 - Luca Signorelli: the *Heaven*. Map of the *giornate* with the paths of the execution sequence.

Fig. 5 - Luca Signorelli: the *Heaven*. Sequence of the *giornate*.


1
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a probable level of the scaffold
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c4
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c5
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c7
c8
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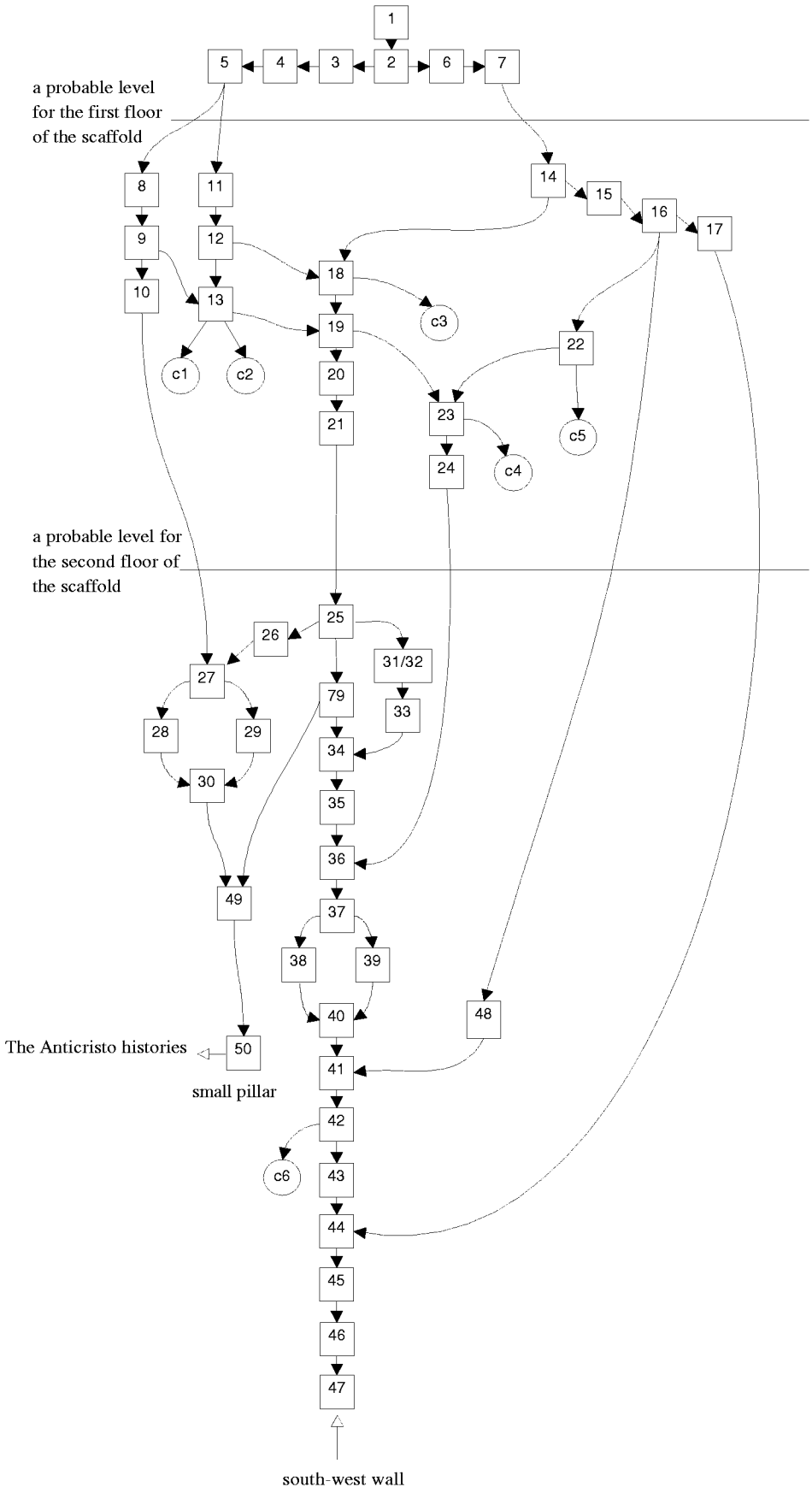
21
c9
28
22
29
23
south-west wall
30
33
34
small pillar
The Resurrection of the body

Figure 3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c4
a probable level for
the second floor of
the scaffold
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48
The Anticristo histories
50
41
small pillar
42
c6
43
44
45
46
47
south-west wall

Figure 5